

A TEXT-BOOK OF  
MACRO AND SEMIMICRO  
QUALITATIVE  
INORGANIC  
ANALYSIS

BY

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FOURTH EDITION



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## PREFACE TO THE FOURTH EDITION

THE text has been exhaustively revised, considerably enlarged and completely reset in the present edition. The opportunity has been taken of rearranging certain sections and chapters which, it is hoped, will enhance the value of the book: thus the technique of semimicro analysis is now incorporated in Chapter II (Experimental Technique of Qualitative Inorganic Analysis). The author's aim has continued to be to provide a text-book of macro and semimicro qualitative inorganic analysis at moderate cost which can be employed by the student continuously throughout his study of the subject. There is some duplication in the chapters devoted to the needs of the elementary student, but it is felt that this method of treatment will assist to lay a firm and sound foundation from the very outset and also retain the individuality of Chapters V and VI. The numerous new tests and procedures have been thoroughly tested in the laboratory.

The following changes and new features in the present edition may be mentioned:

1. The Brönsted-Lowry treatment of acids and bases (I, 5).
2. An extended treatment of activity coefficients and their applications (I, 11 and I, 15).
3. An extended treatment of the determination of  $pH$  (I, 38 and I, 39).
4. Treatment of hydrolysis from the standpoint of the proton theory of acids and bases (I, 42).
5. The description of semimicro apparatus and semimicro analytical operations (II, 3) has been revised in the light of experience in the laboratory during the last eight years. (Since both hand and electric semimicro centrifuges are now comparatively inexpensive, the description of the pressure-filter tube method of filtration has been omitted.)
6. All the group separation tables on the semimicro scale as well as many on the macro scale have been revised; some tables are new. The separation of Group IIA (copper group) and IIB (arsenic group) by the potassium hydroxide method has been included: this procedure has much to commend it

and merits wider application than it has had in the past. The precipitation of Group IV (calcium group) *after* evaporation of the filtrate from Group IIIB (zinc group) to dryness and elimination of all ammonium salts has been adopted as standard practice. {The latter is based upon the work of A. Scheinkman (1931) and of van Nieuwenburg and G. Dulfer (1938); it seems to be insufficiently realised that high concentrations of ammonium salts hinder the complete precipitation of Group IV (calcium group) by ammonium carbonate solution.}

7. The zirconyl nitrate method for the separation of phosphate. {This is based upon the researches of D. J. Cole (1952) in the laboratory of Dr. A. J. Lindsey at the Sir John Cass College; it is superior to most other "phosphate separations" and has therefore been given at the appropriate points in the text.}

8. The reactions of palladous compounds (IX, 7).

9. A short chapter on inorganic paper chromatography. {This account is based largely upon the researches at the Chemical Research Laboratory, Department of Scientific and Industrial Research, Teddington; the writer desires to acknowledge his indebtedness to Dr. F. H. Burstall and Mr. R. A. Wells for their kind help in supplying photographs of paper chromatograms and also certain experimental details.}

The book will be found suitable for students preparing for the General and Honours (Special) B.Sc. degree of the Universities, for other University Examinations of equivalent standard, and for the Associateship of the Royal Institute of Chemistry; also for the General Certificate of Education at Advanced Level, the Preliminary Scientific Examination of the Pharmaceutical Society, for the Ordinary and Higher National Certificates in Chemistry, the various Scholarship Examinations, and for general laboratory use. It is hoped, also, that the volume will be useful to practising analytical chemists.

The author wishes to record his indebtedness to Dr. A. Claassen of Eindhoven for numerous suggestions; to Mr. C. Kyte, B.Sc., for checking the new tests and procedures; to Dr. J. Leicester for the experimental work upon inorganic paper chromatography; to Messrs. W. T. Cresswell, B.Sc., and C. M. Ellis, B.Sc., and Drs. G. H. Jeffery and J. Leicester for reading the galley proofs and for helpful suggestions; and finally to Dr. G. H. Jeffery for his help and advice upon numerous occasions.

The writer would be glad to hear from teachers, analytical chemists and others of any errors which may have escaped his notice; any suggestions whereby the book can be improved will be welcomed.

A. I. VOGEL

Woolwich Polytechnic,

London, S.E.18

*September 1953*

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## CHAPTER I

# THE THEORETICAL BASIS OF QUALITATIVE ANALYSIS

## ELEMENTARY TREATMENT

**Qualitative analysis** has for its object the identification of the constituents of a substance, of mixtures of substances or of solutions, and the manner in which the component elements or groups of elements are combined with one another. **Quantitative analysis** is concerned with the methods of determining the relative proportions of these constituents. It is evident that rigid qualitative analysis must precede the quantitative analysis; the former should give an approximate indication of the relative proportions of the constituents present and should serve as a guide to the methods to be adopted in the latter.

In what follows, the principles underlying the separation of the more commonly occurring elements will be considered. The treatment will be an elementary one and is designed as an introduction to the subject. By its aid it is hoped that the student will be able to appreciate the significance of the operations commonly employed in qualitative analysis. In addition, a knowledge of the principal reactions of the elements and their derivatives is necessary. Chapters III and IV deal with this aspect of the subject. The molecular chemical equations are given throughout. The student should have no difficulty, after studying Sections I, 24 and I, 25 in converting most of these into "ionic equations."

The identification of a substance involves its conversion, usually with the aid of another substance of known composition, into a new compound which possesses characteristic properties. This transformation is called a **chemical reaction**. The substance by means of which this transformation is brought about is termed the **reagent**. One distinguishes between reactions in the **wet way** (*i.e.* those in which a liquid, usually water, is present) and reactions in the **dry way**; the former are by far the more important and will therefore be studied in greater detail.

## REACTIONS OF INORGANIC SUBSTANCES IN AQUEOUS SOLUTION

The reactions employed in qualitative analysis are largely the reactions of inorganic acids, bases and salts with each other in aqueous solution. Other solvents are rarely employed except for special operations. It is therefore necessary to have a general knowledge of the conditions that exist in such solutions.

### THEORY OF ELECTROLYTIC DISSOCIATION

**I, 1. Electrolytes and Non-Electrolytes.**—A solution is the homogeneous product obtained when a substance is dissolved in water (or any other liquid); the dissolved substance is known as the **solute**, and the water (or other liquid) in which the solute is dissolved is called the **solvent**. Substances can be divided into two main classes according to the behaviour of their aqueous solutions to an electric current. In the first class one has those which conduct the electric current and are decomposed thereby; the second class is composed of those which yield non-conducting solutions. The former are termed **electrolytes**, and these include acids, bases and salts; the latter are designated **non-electrolytes**, and are exemplified by cane sugar, mannose, glucose, glycerine, ethyl alcohol and urea. It must be pointed out that a substance which is an electrolyte in water, *e.g.* sodium chloride, may not yield a conducting solution in another solvent such as ether or hexane. Furthermore, electrolytic character is not confined to solutions; it is also manifested by fused salts.

**I, 2. Electrolysis and Ions.**—Pure water is a very poor conductor of electricity but, as already stated, when acids, bases or salts are dissolved in it, the resultant solution not only conducts the electric current but is also simultaneously decomposed. The decomposition is called **electrolysis**. Thus, if an electric current from, say, a battery is passed through hydrochloric acid, the hydrogen chloride is split up into hydrogen and chlorine. The hydrogen is liberated at the electrode by which the current leaves the solution (the negative electrode or **cathode**) whilst the chlorine is liberated at the electrode by which the current enters the solution (the positive electrode or **anode**). This behaviour is a general one for electrolytes—for the present it is assumed that no secondary changes occur at the electrodes—and it is obvious that the part of the electrolyte



moving to the cathode must be positively charged and that moving to the anode must likewise be negatively charged. Faraday termed the charged components of the electrolyte

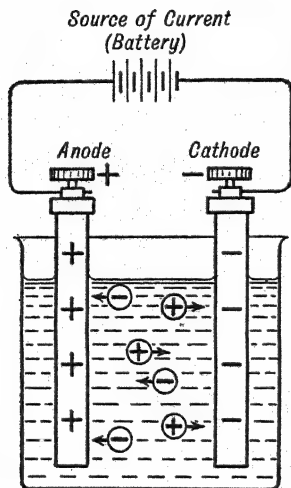


Fig. I, 2, 1

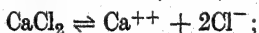
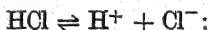
ions; the positively and negatively charged ions were called **cations** and **anions** respectively. A diagrammatic figure of electrolysis is shown in Fig. I, 2, 1.

**I, 3. Some Properties of Aqueous Solutions.**—It has been found experimentally that equimolecular quantities of non-electrolytes, dissolved in the same weight of solvent, have the same effect upon the lowering of vapour pressure, the depression of freezing point and the elevation of boiling point. The determination of any of these quantities for a solution therefore enables one to calculate the molecular weight of the dissolved substance provided the change produced by one molecular weight in a known weight of solvent is known. Thus the freezing point of water is lowered by  $1.86^{\circ}\text{C}$  by the molecular weight of any non-electrolyte dissolved in 1000 grams; the boiling point is similarly raised by  $0.51^{\circ}\text{C}$ .

Abnormal results were obtained with electrolytes. Those of the sodium chloride type gave a depression of freezing point of about twice the expected or normal magnitude, whilst with compounds of the type of calcium chloride or sodium sulphate the depression of freezing point was approximately three times

that produced by a non-electrolyte of the same molecular concentration.

It was to explain the abnormal vapour pressures, freezing points and boiling points of aqueous solutions of electrolytes that Arrhenius in 1887 put forward his theory of electrolytic dissociation or ionisation. According to this theory, all electrolytes when dissolved in water are decomposed or dissociated into charged atoms or groups of atoms (ions). The extent of this dissociation or ionisation increases with dilution, and at very great dilutions it is practically complete. For every concentration there is a state of equilibrium between the undissociated molecules and the ions; the process is a reversible one. The ionisation of compounds may therefore be represented by:



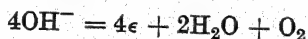
The ions carry positive and negative charges and, since the solution is electrically neutral, the total number of positive charges must be equal to the total number of negative charges. The number of charges carried by an ion is equal to the valency of the atom or radical.

The abnormal results referred to above now receive a simple explanation if it be assumed that the effect of each ion upon the vapour pressure, freezing point or boiling point is equivalent to that of a molecule of a non-electrolyte. Sodium chloride yields two ions in aqueous solution, so that the nearly double depression of freezing point obtained in dilute solution would appear to indicate considerable dissociation. The results for sodium sulphate and calcium chloride are similarly accounted for. It is evident that precise measurements of this "abnormality" may be employed to calculate the extent of ionisation or the degree of dissociation. Another method for determining this quantity, dependent upon the measurement of electrical conductivity, will be discussed in a subsequent section.

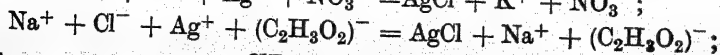
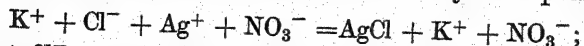
The phenomena of electrolysis also receive a simple explanation on the basis of the theory of electrolytic dissociation. The conducting power of aqueous solutions of electrolytes is due to the ions which transport the current through the solution. Returning to the example of hydrochloric acid already considered, it is clear that if two inert electrodes, say

of platinum, connected to a source of current, be introduced into the solution, the positively charged hydrogen ion  $H^+$  will travel to the cathode from which it will take up one electron, become converted into a neutral hydrogen atom and be discharged. The negatively charged chlorine ion  $Cl^-$  will be attracted to the anode; here it will give up its charge, become neutral and be liberated as the free gas. The discharge of the ions is accompanied by a simultaneous dissociation of the electrolyte in order to maintain the equilibrium.

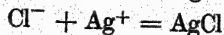
The phenomenon is not always as simple as for hydrochloric acid. The ions are not always discharged at the respective electrodes; they may also react with the electrodes themselves or with the electrolyte or if the potential required to discharge either of the ions be greater than that necessary for the discharge of the ions of water  $H^+$  and  $OH^-$  ( $H_2O \rightleftharpoons H^+ + OH^-$ ), either of the latter may be preferentially discharged. Thus in the electrolysis of sodium chloride solution, chlorine is evolved at the anode and the sodium initially formed at the cathode reacts with the water liberating hydrogen; with a mercury cathode, however, the sodium dissolves in the mercury and an amalgam is formed. The electrolysis of a solution of sodium sulphate ( $Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{--}$ ) results in the liberation of hydrogen at the cathode and oxygen at the anode. The latter arises from the circumstance that the sulphate ion  $SO_4^{--}$  requires a higher potential for its discharge than does the hydroxyl ion  $OH^-$  and hence the latter is discharged in accordance with the equation:



**I, 4. Reactions of Ions.**—Most of the wet reactions employed in qualitative analysis are reactions of the ions. It is an experimental fact that the compounds of most metals with chlorine (chlorides), which are soluble in water, yield a white precipitate of silver chloride when treated with a solution of silver nitrate. This is because all chlorides give rise to the chloride ion  $Cl^-$  in aqueous solution, and this reacts with the silver ion  $Ag^+$  originating from the silver nitrate solution. In a similar manner all silver salts, which dissociate in aqueous solution, will give the same precipitate when chloride ions are added to their solutions. The reactions may be represented:



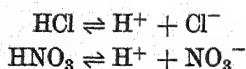
or



Thus the precipitation of the highly insoluble silver chloride is due to the combination between silver and chloride ions. These ions react independently of the other ions with which they were originally associated in the solid state.

When a solution of potassium chlorate is added to one of silver nitrate, no precipitate of silver chloride is obtained, because potassium chlorate furnishes  $K^+$  ions and  $ClO_3^-$  ions in solution but no  $Cl^-$  ions. Silver nitrate, dissolved in ethyl alcohol, does not yield a precipitate with chlorobenzene  $C_6H_5Cl$  or with carbon tetrachloride  $CCl_4$  in alcoholic solution, although it does so with sodium chloride solution. The sodium chloride is dissociated to a small extent in alcoholic solution; the chlorobenzene and carbon tetrachloride not at all.

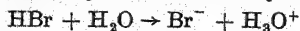
**I, 5. Theory of Acids and Bases.**—An *acid* is most simply defined (after Arrhenius) as a substance which, when dissolved in water, undergoes dissociation with the formation of hydrogen ions as the only positive ions:



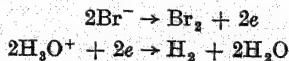
Actually hydrogen ions  $H^+$  (or protons) do not exist in the free state in aqueous solution. Each proton is bound to one water molecule by coordination with a pair of free or lone electrons on the oxygen of the water,  $H^+ \leftarrow OH_2$  or  $H_3O^+$ ; its formation is similar to that of the ammonium ion  $NH_4^+$ , which is a co-ordination of a proton with a pair of electrons on the nitrogen in ammonia,  $H^+ \leftarrow NH_3$ . The  $H_3O^+$  ion is termed the **hydroxonium**, **oxonium** or **hydronium** ion: the first of these names will be employed.

The experimental evidence for the existence of the hydroxonium ion in aqueous solution includes the following:

(i) Liquid sulphur dioxide (at  $-30^\circ$ ) dissolves water to a small extent and hydrogen bromide in larger quantity but neither of these solutions alone forms a conducting solution. The solution of hydrogen bromide in liquid sulphur dioxide will dissolve exactly one molecule of water per molecule of hydrogen bromide giving a highly conducting solution. These observations are readily accounted for by the reaction:

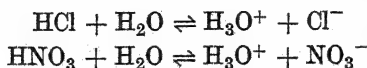


Furthermore, when the solution is electrolysed, bromine is liberated at the anode and hydrogen is evolved at the cathode; also the solution near the cathode gains one molecule of water for each hydrogen ion deposited at the cathode:



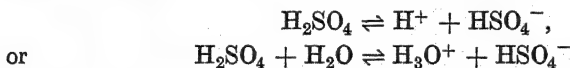
(ii) X-ray examination of crystalline perchloric acid monohydrate indicates that it forms an ionic lattice  $[\text{H}_3\text{O}^+][\text{ClO}_4^-]$ , *i.e.*  $\text{H}_3\text{O} \cdot \text{ClO}_4 \rightarrow \text{H}_3\text{O}^+ + \text{ClO}_4^-$ : it is isomorphous with ammonium perchlorate  $[\text{NH}_4^+][\text{ClO}_4^-]$ .

The above equations are more accurately expressed by:

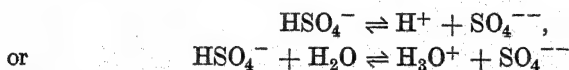


The dissociation may be attributed to the great tendency of the free hydrogen ions  $\text{H}^+$  or protons to combine with water to form hydroxonium ions. Hydrochloric and nitric acids are almost completely dissociated in aqueous solution in accordance with the above equations; this is readily detected by freezing point measurements.

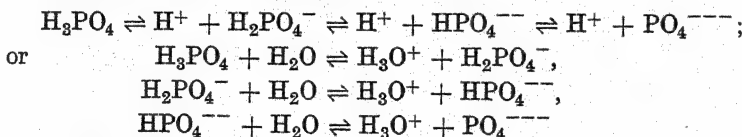
**Polybasic acids** dissociate in stages. In sulphuric acid, the first hydrogen atom is almost completely ionised:



The second hydrogen atom is only partially dissociated, except in very dilute solution:



Phosphoric acid also dissociates in stages:

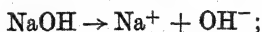


The successive stages of dissociation are known as the primary, secondary and tertiary dissociation respectively. As already mentioned, these do not take place to the same degree. The primary dissociation is always greater than the secondary, and the secondary very much greater than the tertiary.

Acids of the type of acetic acid  $\text{H} \cdot \text{C}_2\text{H}_3\text{O}_2$ , give an almost normal freezing point depression in aqueous solution; the extent of dissociation is accordingly small. It is usual, therefore, to distinguish between acids which are completely or almost completely dissociated in solution and those which are only slightly dissociated. The former are termed **strong acids** (examples: hydrochloric, nitric and iodic acids, primary dissociation of sulphuric acid) and the latter are called **weak acids**.

(examples: acetic acid, secondary and tertiary ionisation of phosphoric acid, carbonic acid, boric acid and hydrogen sulphide). There is, however, no sharp division between these classes. Methods for the measurement of the relative strengths of acids are described in Section I, 12.

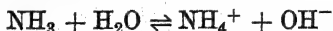
A **base** is most simply defined (after Arrhenius) as a substance which, when dissolved in water, undergoes dissociation with the formation of hydroxide ions  $\text{OH}^-$  as the only negative ions. Thus sodium hydroxide, potassium hydroxide and other metallic hydroxides are almost completely dissociated in aqueous solution:



these are **strong bases**. Aqueous ammonia solution, however, is a **weak base**. Only a small concentration of hydroxide ions is produced in aqueous solution. Arrhenius assumed the intermediate formation of ammonium hydroxide by the partial hydration of ammonia:



It is more usual to write the reaction as:



The above classical definitions of acids and bases proved to be of very limited application, although they suffice for many applications in qualitative inorganic analysis. These limitations are apparent, for example, in the field of non-aqueous solvents. Thus, if potassium hydroxide is dissolved in ethyl alcohol, the solution will contain hydroxide ions, just as in water: by dissolving potassium ethoxide in the same solvent, a solution with stronger basic properties is obtained and this contains ethoxide ions ( $\text{OC}_2\text{H}_5^-$ ) in place of hydroxide ions. With ethyl alcohol as solvent, it would seem more logical to define bases in terms of the ethoxide ion rather than in terms of the hydroxide ion. Similarly, in liquid ammonia the strongest bases are the metallic amides  $\text{MeNH}_2$ , and the characteristic basic ion is the amide ion  $\text{NH}_2^-$ .

A more general definition of acids and bases was proposed almost simultaneous and independently in 1923 by J. N. Brønsted and T. M. Lowry. They define an *acid* as any substance (in either the molecular or ionic state) which donates protons ( $\text{H}^+$ ), and a *base* as any substance (molecular or ionic) which accepts protons. This can be expressed by the scheme:



where  $A$  and  $B$  are termed a **conjugate** (or **corresponding**) **acid-base pair**. It is important to realise that the symbol  $H^+$  in this definition represents the bare proton or unsolvated hydrogen ion, and hence the new definition is independent of the solvent. The equation expresses a hypothetical scheme for defining the acid and base, and not a reaction which can actually take place. The dissociation of an acid to yield  $H^+$  is conditioned by the presence of a base, *i.e.* a substance capable of accepting the liberated  $H^+$ .

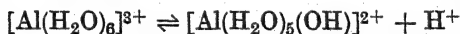
The Brönsted-Lowry definition of an acid includes:

(a) the uncharged molecules known as acids in the classical dissociation theory, *e.g.*  $HCl$ ,  $HNO_3$ ,  $H_2SO_4$ ,  $CH_3.COOH$ , etc.;

(b) anions like  $HSO_4^-$ ,  $H_2PO_4^-$  and  $HOOC.COO^-$ , which occur in acid salts;

(c) the ammonium ion by virtue of the tendency represented by  $NH_4^+ \rightleftharpoons NH_3 + H^+$ , and the hydroxonium ion ( $H_3O^+ \rightleftharpoons H_2O + H^+$ )—these are examples of **cation acids**; and

(d) cations, like the hydrated aluminium and other metallic ions

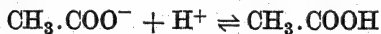


For bases, the new definition is concerned with the ability of accepting a proton and not with the production of the hydroxide or some similar ion. The following are included:

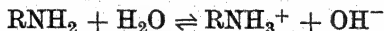
(a) uncharged molecules (ammonia and the amines) by virtue of the reaction  $RNH_2 + H^+ \rightleftharpoons RNH_3^+$ ;

(b) metallic hydroxides, due to the production of the hydroxide ion— $OH^- + H^+ \rightleftharpoons H_2O$ .

The hydroxide ion is one example of an anion base: other examples are the anions of all weak acids. Thus the acetate ion is a weak base:



It is important to note that the familiar strong bases according to the classical definition, such as the alkali and alkaline earth hydroxides, are invariably ionic in nature even in the solid state. The basic nature of these strong bases is due to the  $OH^-$  ions which are always present in the solid state or in aqueous solution, and interaction with the solvent is not an essential preliminary as for weaker bases, such as those of the ammonia ( $RNH_2$ ) type:

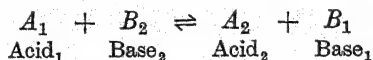


Some substances can function both as acids and bases, and



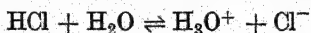
are called amphoteric electrolytes or **ampholytes**:  $\text{H}_2\text{O}$ ,  $\text{HCO}_3^-$  and  $\text{H}_2\text{PO}_4^-$  are examples.

As already pointed out, the equation  $A \rightleftharpoons B + \text{H}^+$  does not represent a reaction which can actually take place: otherwise expressed, the free proton, because of its small size and the intense electric field surrounding it, will have a great affinity for other molecules, especially those with unshared electrons and therefore cannot exist as such to any appreciable extent in an aqueous or other basic solvent. The acceptor of a proton is a base. Thus if one writes the two equations  $A_1 \rightleftharpoons B_1 + \text{H}^+$  and  $B_2 + \text{H}^+ \rightleftharpoons A_2$ , one obtains:

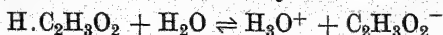


This represents the transfer of a proton from  $A_1$  to  $B_2$  and from  $A_2$  to  $B_1$ . Reactions between acids and bases are therefore often called **protolytic reactions**. The conjugate acid and base are designated by the same subscript.

It is of interest to examine the mechanism of the reaction which occurs when strong and weak acids are dissolved in water as illustrated by hydrochloric acid and by acetic acid respectively. Hydrogen chloride in the gaseous or pure liquid state does not conduct the electric current, and possesses all the properties of a covalent compound. When the gas is dissolved in water, the resulting solution is found to be an excellent conductor of electricity and therefore contains a high concentration of ions. Evidently the water, behaving as a base, has reacted with the hydrogen chloride to form hydroxonium and chloride ions:



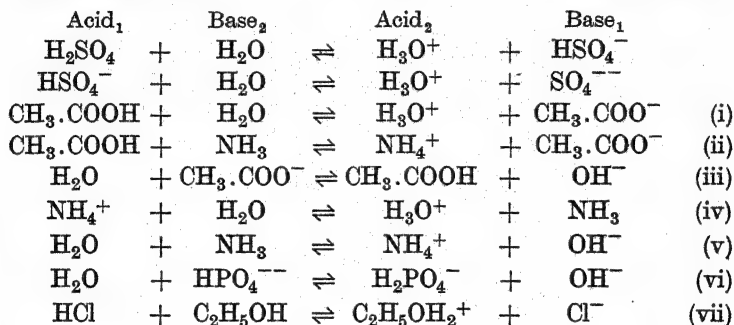
The reaction proceeds almost entirely towards the right, indicating that the ability of water to combine with protons is very much greater than the tendency of chloride ions to combine with  $\text{H}^+$ , i.e. water is a stronger base than chloride ion. When acetic acid is dissolved in water, the resulting solution has a comparatively low conductivity indicating that the concentration of ions is relatively low. The reaction:



proceeds only slightly towards the right, and it is evident that the acetate ion has a more powerful attraction for protons than the chloride ion, i.e.  $\text{C}_2\text{H}_3\text{O}_2^-$  is a stronger base than  $\text{Cl}^-$ . The ionisation of an acid thus depends upon the readiness with which the solvent can take up protons as compared with the anion of the acid. An acid, like hydrogen chloride, which gives

up  $H^+$  readily to the solvent to yield a solution with a high concentration of  $H_3O^+$  is termed a **strong acid**. An acid, like acetic acid, which gives up its protons less readily affording a solution with a relatively low concentration of  $H_3O^+$  is called a **weak acid**. It is clear, therefore, that if the acid is strong, its conjugate base must be weak; if the acid is weak, the conjugate base is strong, *i.e.* possesses a powerful tendency to combine with  $H^+$ .

Some examples of protolytic reactions are collected below:



Reaction (i) represents the dissociation of acetic acid in water; (ii) the neutralisation of acetic acid by ammonia *or* the hydrolysis of ammonium acetate solution; (iii) the hydrolysis of an alkali acetate solution *or* the neutralisation of acetic acid by an alkali hydroxide; (iv) the hydrolysis of an ammonium salt *or* the neutralisation of ammonia by a strong acid; (v) the dissociation of ammonia in water; (vi) the hydrolysis of a secondary phosphate *or* the neutralisation of a primary phosphate with an alkali hydroxide; and (vii) ethyl alcohol functioning as a base and yielding the conjugate acid  $C_2H_5OH_2^+$ . Some of these reactions are discussed in greater detail in Section I, 42.

**Salts.** The structure of numerous salts in the solid state has been investigated by means of X-rays and by other methods, and it has been shown that ions are actually present in the solid state. Sodium chloride, for instance, is built up of sodium ions and chlorine ions so arranged that each ion is surrounded symmetrically by six ions of the opposite sign; the crystal lattice is held together by electrostatic forces due to the charges upon the ions. It is not surprising, therefore, that when salts are dissolved in a solvent of high dielectric constant such as water, they are completely dissociated. The complete dissociation of salts in aqueous solution is the modern view and is now almost universally accepted. There are, however, some exceptions,

and these have, in some cases, been supported by X-ray measurements. Feebly dissociated salts (weak electrolytes) are exemplified by mercuric chloride, mercuric cyanide, lead acetate and the cadmium halides.

**I, 6. Experimental Determination of the Approximate Degree of Dissociation.**—The degree of dissociation of an electrolyte in an aqueous solution may be computed (after Arrhenius) either from the freezing point or from the electrical conductivity. Let us consider the **freezing point method** first. If 1 gram molecule of a binary electrolyte is dissolved in 1 litre of water and if a fraction  $\alpha$  of the gram molecule is dissociated, the solution will contain  $(1 - \alpha)$  gram molecule of the undissociated electrolyte and  $2\alpha$  gram molecules of ions. The total concentration of the solute will be  $(1 - \alpha) + 2\alpha = (1 + \alpha)$  gram molecules. If  $\Delta$  (*theory*) is the depression of freezing point produced at this concentration by a non-electrolyte (*i.e.* when no dissociation occurs), and  $\Delta$  (*obs.*) is the observed depression of freezing point, then

$$\Delta(\text{obs.})/\Delta(\text{theory}) = (1 + \alpha)/1 = i \quad \text{or} \quad \alpha = i - 1$$

Similarly, if the molecule of the electrolyte gives rise to  $n$  ions upon dissociation, the increase in the number of solute particles in the solution will be in the ratio of  $\{1 + (n - 1)\alpha\}/1$ , or

$$\alpha = (i - 1)/(n - 1). \quad \text{Dissociation is complete when } i = n.$$

Let us now study the **conductivity method**. The electric current is transferred through the solution by means of the ions, hence the conductance at any temperature, measured in a definite way, will depend upon the degree of ionisation. The **specific resistance** or **resistivity**  $\rho$  of a solution is the resistance in ohms, measured between parallel faces, of a cube of 1 centimetre side. The reciprocal of the specific resistance or resistivity is called the **specific conductance** or **conductivity**, and is generally represented by the Greek symbol kappa ( $\kappa$ ). It is measured in "reciprocal ohms" or **mhos** (mho = ohm written backwards),  $\kappa = 1/\rho$ . For electrolytic solutions, it is more convenient to employ the **equivalent conductance** or the **equivalent conductivity** (frequently designated by the Greek symbol lambda  $\Lambda$ ) for purposes of comparison. The latter is the conductance of a solution which contains 1 gram equivalent of the solute between two electrodes of indefinite size, 1 centimetre apart. The specific conductance and equivalent conductance are connected by the relation:

$$\Lambda = \kappa V = \kappa/c,$$

where  $V$  is the volume in c.c. containing 1 gram equivalent of the solute and  $c$  is the concentration in gram equivalents per cubic centimetre.

The discovery that the equivalent conductance of aqueous solutions of electrolytes increases with dilution and ultimately reaches a limiting value, was made by Kohlrausch. The Arrhenius theory sought to account for this by assuming that the degree of dissociation increases with increase of dilution until at very great dilutions dissociation is complete. The limiting conductance corresponds to complete dissociation; it is represented by  $\Lambda_0$  (when referring to concentrations), or  $\Lambda_\infty$  (when referring to dilutions). The degree of dissociation  $\alpha$ , at any concentration  $c$ , is given by  $\alpha = \Lambda_c/\Lambda_0$ , where  $\Lambda_c$  is the equivalent conductance at that concentration. Some results for the degree of dissociation  $\alpha$ , deduced from freezing point and conductivity data, are collected in Table I, 6, 1: it will be noted that the agreement is only approximate up to about 0.1N and it may be stated that in more concentrated solutions the two values differ considerably.

TABLE I, 6, 1. DEGREE OF DISSOCIATION OF ELECTROLYTES BY FREEZING AND BY CONDUCTIVITY METHODS

Substance	Concentration G. equiv./litre	$\alpha$ from freezing point	$\alpha$ from conductivity	No. of ions for one molecule, $n$
KCl	0.01	0.946	0.943	2
	0.02	0.915	0.924	
	0.05	0.890	0.891	
	0.10	0.862	0.864	
BaCl <sub>2</sub>	0.001	0.949	0.959	3
	0.01	0.903	0.886	
	0.10	0.798	0.754	
K <sub>2</sub> SO <sub>4</sub>	0.001	0.939	0.957	3
	0.01	0.887	0.873	
	0.10	0.748	0.716	
K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	0.001	0.946	0.930	4
	0.01	0.865	0.822	
	0.10	0.715	—	

The variation of equivalent conductance with concentration for a number of electrolytes at 25°C is shown in Table I, 6, 2.

TABLE I, 6, 2. EQUIVALENT CONDUCTANCES AT 25°C

Concn.	KCl	NaCl	HCl	NaOH	KOH	Na. $C_2H_3O_2$	H. $C_2H_3O_2$
0.0001	149.2	125.3	—	—	—	—	—
0.0002	—	—	—	—	—	—	104.0
0.0005	148.3	124.3	422.2	246.5	270.1	89.4	64.5
0.001	147.5	123.5	421.1	244.7	268.2	88.7	48.7
0.002	146.5	122.2	419.2	242.5	266.2	87.7	35.2
0.005	144.2	119.8	414.9	238.8	262.1	85.7	22.8
0.01	141.6	117.8	410.5	234.5	258.9	83.7	16.2
0	150.1	126.2	423.7	260.9	283.9	91.3	388.6

Electrolytes which are largely ionised in solution are called **strong electrolytes**, whilst those which are only slightly ionised are termed **weak electrolytes**. Table I, 6, 3 gives the degree of ionisation or fraction of electrolyte dissociated,  $\alpha$ , as determined from the conductivity in 0.1N solution.

TABLE I, 6, 3. APPARENT DEGREE OF IONISATION IN 0.1N AQUEOUS SOLUTIONS FROM CONDUCTIVITY DATA

Acids		Salts	
Hydrochloric ( $H^+$ , $Cl^-$ )	0.92	Potassium chloride ( $K^+$ , $Cl^-$ )	0.86
Nitric ( $H^+$ , $NO_3^-$ )	0.92	Sodium chloride ( $Na^+$ , $Cl^-$ )	0.86
Sulphuric ( $H^+$ , $HSO_4^-$ )	0.61	Potassium nitrate ( $K^+$ , $NO_3^-$ )	0.82
Phosphoric ( $H^+$ , $H_2PO_4^-$ )	0.28	Silver nitrate ( $Ag^+$ , $NO_3^-$ )	0.82
Hydrofluoric ( $H^+$ , $F^-$ )	0.085	Sodium acetate ( $Na^+$ , $CH_3COO^-$ )	0.80
Acetic ( $H^+$ , $CH_3COO^-$ )	0.013	Barium chloride ( $Ba^{++}$ , $2Cl^-$ )	0.75
Carbonic ( $H^+$ , $HCO_3^-$ )	0.0017	Potassium sulphate ( $2K^+$ , $SO_4^{--}$ )	0.73
Hydrosulphuric ( $H^+$ , $HS^-$ )	0.0007	Sodium carbonate ( $2Na^+$ , $CO_3^{--}$ )	0.70
Hydrocyanic ( $H^+$ , $CN^-$ )	0.0001	Zinc sulphate ( $Zn^{++}$ , $SO_4^{--}$ )	0.40
Boric ( $H^+$ , $H_2BO_3^-$ )	0.0001	Copper sulphate ( $Cu^{++}$ , $SO_4^{--}$ )	0.39
		Mercuric chloride ( $Hg^{++}$ , $2Cl^-$ )	<0.01
		Mercuric cyanide ( $Hg^{++}$ , $2CN^-$ )	very small
Bases			
	Sodium hydroxide ( $Na^+$ , $OH^-$ )	0.91	
	Potassium hydroxide ( $K^+$ , $OH^-$ )	0.91	
	Barium hydroxide ( $Ba^{++}$ , $2OH^-$ )	0.81	
	Ammonia ( $NH_4^+$ , $OH^-$ )	0.013	

It should be mentioned that although the results for strong electrolytes have been considerably modified (their ionisation is now regarded as complete—see Section I, 8), the general picture presented by the Table is still significant in so far as

the broad difference between strong and weak electrolytes and also between individual weak electrolytes are concerned.

For strong electrolytes, the limiting conductance  $\Lambda_0$  may be determined by extending the measurements to low concentrations and then extrapolating the conductivity-concentration curve to zero concentration. For weak electrolytes, such as acetic acid and ammonia, this method cannot be employed since the dissociation is nowhere near complete at the lowest concentrations at which measurements can be conveniently made (*ca.* 0.0001*N*). Another method is, however, available for estimating  $\Lambda_0$ . This is described in the following section.

**I, 7. The Independent Migration of Ions.**—As a result of a prolonged and careful study of the conductance of salt solutions down to low concentrations, Kohlrausch found that the equivalent conductance of an electrolyte is made up of the sum of the limiting equivalent conductances of the component ions. This permits one to predict  $\Lambda_0$  by adding together numbers which are characteristic of the ions in the solution. The relation is:

$$\Lambda_0 = \lambda_{0c} + \lambda_{0a},$$

where  $\lambda_{0a}$  and  $\lambda_{0c}$  are the limiting conductances or *mobilities* of the anion and cation respectively. The ionic mobilities are computed from  $\Lambda_0$  with the aid of *transport numbers*; these represent the fraction of the current carried by the cation and anion respectively, and are obviously proportional to their respective speeds. (For a fuller discussion of transport numbers, the student is referred to text-books of physical chemistry.) Thus for potassium chloride at 18°,  $\Lambda_0 = 130.1$ ,  $n_a$  the anion transport number is 0.503 (after Kohlrausch and Maltby), hence

$$\lambda_{0a} = \lambda_{Cl^-} = 0.503 \times 130.1 = 65.5,$$

and  $\lambda_{0c} = \lambda_{K^+} = 0.497 \times 130.1 = 64.6$

When one pair of mobilities is known, others may be computed from the relation, also discovered by Kohlrausch, that the difference between the values of  $\Lambda_0$  for two anions is independent of the cation and *vice versa*. In this manner, a table of mobilities can be constructed. Some limiting ionic mobilities at 18°C and 25°C are collected in Table I, 7, 1. This may be utilised for the determination of the limiting conductance of any electrolyte. Its particular value is for weak electrolytes

TABLE I, 7, 1. LIMITING IONIC MOBILITIES AT 18°C AND 25°C

18°C				25°C			
H <sup>+</sup>	317.0	OH <sup>-</sup>	174.0	H <sup>+</sup>	348.0	OH <sup>-</sup>	210.8
Na <sup>+</sup>	43.5	Cl <sup>-</sup>	65.5	Na <sup>+</sup>	49.8	Cl <sup>-</sup>	76.4
K <sup>+</sup>	64.6	NO <sub>3</sub> <sup>-</sup>	61.8	K <sup>+</sup>	73.4	IO <sub>3</sub> <sup>-</sup>	42.0
Ag <sup>+</sup>	54.4	Br <sup>-</sup>	67.7	Ag <sup>+</sup>	61.9	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	40.6
1/2 Ca <sup>++</sup>	52.2	I <sup>-</sup>	66.1				
1/2 Sr <sup>++</sup>	51.7	F <sup>-</sup>	46.8				
1/2 Ba <sup>++</sup>	55.0	ClO <sub>3</sub> <sup>-</sup>	55.0				
1/2 Pb <sup>++</sup>	61.6	IO <sub>3</sub> <sup>-</sup>	34.0				
1/2 Cd <sup>++</sup>	46.5	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	32.5				
1/2 Zn <sup>++</sup>	46.0	1/2 SO <sub>4</sub> <sup>--</sup>	68.3				
1/2 Cu <sup>++</sup>	45.9	1/2 C <sub>2</sub> O <sub>4</sub> <sup>--</sup>	61.1				

where  $\Lambda_0$  cannot be determined by direct extrapolation. Thus for acetic acid at 25°,

$$\Lambda_0 = \lambda_{\text{C}_2\text{H}_3\text{O}_2^-} + \lambda_{\text{H}^+} = 40.6 + 348.0 = 388.6$$

The degree of dissociation at any concentration  $c$  can then be calculated from the relation  $\alpha = \Lambda_c/\Lambda_0$ , where  $\Lambda_c$  is the equivalent conductance at that concentration. A few typical results, calculated in this manner, are collected in Table I, 7, 2.

TABLE I, 7, 2. DISSOCIATION OF ACIDS AT 25°C

	Degree of Dissociation	
	0.5N	0.001N
<i>Strong Acids</i>		
Hydrochloric acid	0.862	0.993
Sulphuric acid (primary ionisation)	0.536	0.960
Nitric acid	0.862	0.997
Trichloroacetic acid	0.760	0.994
<i>Weak acids</i>		
Acetic acid	0.006	0.126
Carbonic acid	0.0008	0.017
Hydrocyanic acid	0.00005	0.0011

It is evident that the degree of dissociation varies considerably both with the nature of the acid and with the concentration.



The strengths of acids can be *roughly* compared in terms of  $\alpha$  at any given concentration. This method of comparison divides the acids into two main groups: **strong acids**, which are largely dissociated, and **weak acids**, which are feebly dissociated in aqueous solution. Considerable variations occur amongst the weak acids, and more accurate methods for the comparison of their strengths will be discussed under the law of mass action (Section I, 9).

**I, 8. Theory of Complete Ionisation. Interionic Attraction Theory of Debye, Hückel and Onsager.**—It has already been pointed out that strong electrolytes, particularly salts and bases, are completely dissociated in aqueous solution. How then is one to explain the increasing equivalent conductance with decreasing concentration? We have seen that Arrhenius ascribed this to the increasing degree of dissociation, the mobilities of the ions at all concentrations being assumed constant. This classical view can now no longer be held to possess any significance for strong electrolytes. Debye and Hückel in 1923 and Onsager in 1925 accepted the complete dissociation theory, and attributed the changes in conductance with dilution (and also the associated changes in osmotic activity in dilute solutions) to the electrical forces between the ions. Owing to the interionic forces, each ion will build up an "atmosphere" of ions of opposite sign. When an electromotive force is applied, the ionic "atmosphere" will be unsymmetrical, for the ion has to build up a new ionic "atmosphere" in front, whilst the "atmosphere" behind the moving ion will be dispersed. The dispersal of the ionic "atmosphere," however, requires a certain amount of time ("time of relaxation"), and hence there will always be, in the rear of the moving ion, an excess of ions of opposite sign as a result of which the mobility will be diminished. Further, the motion of, say, a positively charged reference ion will be subject to a retardation by the movement of the negative ions in the opposite direction, and the effect will be that of a viscous electrical drag ("electrophoretic effect"). In short, the speed of the ions will be diminished because of the attractive forces exerted by the ions constituting the "atmosphere" of opposite sign. The attractive forces will clearly be greater the more concentrated the solution, since the ions are brought closer together. Consequently the mobility of the ions will decrease with increasing concentration. At extreme dilutions the interionic forces will become negligibly small owing to the relatively great distance between the ions, and the mobilities

will approach a maximum value. The change in equivalent conductivity is thus attributed, not as in the Arrhenius theory to changes in the degrees of dissociation or to changes in the number of ions, but to variations in the velocities of the ions due to interionic forces. Debye, Hückel and Onsager have deduced an expression which accounts satisfactorily for the variation of the equivalent conductance with concentration of strong electrolytes from the lowest concentration to about  $0.002N$ : it may be expressed in the form that  $\Lambda_c$  is proportional to the square root of the concentration. At higher concentrations deviations occur, and many, at present, empirical assumptions are introduced to express the relationship between  $\Lambda_c$  and the concentration over a larger concentration range. The deviations may be regarded as due to some form of ionic association, such as the formation of ionic doublets which may behave, in some respects, as unionised molecules. The extent to which this occurs will depend upon the interionic forces and upon the chemical nature of the ions of the solvent, since many ions possess a tendency to undergo solvation, *i.e.* to combine with the molecules of the solvent.

It is important to realise that whilst complete dissociation occurs with strong electrolytes, this does not mean that the *effective concentrations* of the ions are the same at all concentrations, for if this were the case, the osmotic properties of aqueous solutions could not be accounted for. The variation of osmotic properties is ascribed to changes of the "*activity*" of the ions; these are dependent upon the electrical forces between the ions. Expressions for the variations of the activity or of related quantities, applicable to dilute solutions, have also been deduced from the Debye-Hückel-Onsager theory. Further consideration of the conception of "*activity*" will be given in the following section.

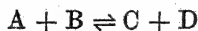
The ratio  $\Lambda_c/\Lambda_0$  on the modern complete ionisation theory no longer gives the degree of ionisation  $\alpha$  for a strong electrolyte (for which  $\alpha = 1$ ): it has been named the **conductivity coefficient** or **conductance ratio**. It does give the approximate degree of dissociation for weak electrolytes, but even here there is a slight ion interaction and a correction may be applied with the aid of the Debye-Hückel-Onsager theory.

## I, 9. THE LAW OF MASS ACTION

Guldberg and Waage in 1867 clearly stated the law of mass action in the form: the velocity of a chemical reaction at

constant temperature is proportional to the product of the concentrations of the reacting substances. The concentrations are usually expressed in gram molecules per litre. On applying the law to homogeneous systems, *i.e.* to systems in which all reacting molecules are present in one phase, for example in solution, one can arrive at a mathematical expression for the conditions of equilibrium in a **reversible reaction**.

Consider first the simple reversible reaction at constant temperature:



The velocity with which A and B react is proportional to their concentrations, or

$$v_1 = k_1 \times [A] \times [B],$$

where  $k_1$  is a constant known as the **velocity coefficient**, and the square brackets in heavy type indicate the molecular concentrations of the substance enclosed within the brackets. Similarly, the velocity with which the reverse reaction occurs is given by

$$v_2 = k_2 \times [C] \times [D]$$

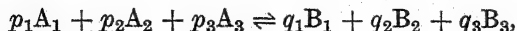
At equilibrium, the velocities of the reverse and forward reactions will be equal (the equilibrium is a dynamic and not a static one) and therefore  $v_1 = v_2$ ,

$$\text{or} \quad k_1 \times [A] \times [B] = k_2 \times [C] \times [D],$$

$$\text{or} \quad \frac{[C] \times [D]}{[A] \times [B]} = \frac{k_1}{k_2} = K$$

$K$  is the **equilibrium constant**; it will vary somewhat with the temperature and pressure, but such variations are of relatively little importance in qualitative analysis.

The expression may be generalised. For a reversible reaction represented by:



where  $p_1, p_2, p_3$  and  $q_1, q_2, q_3$  are the number of molecules of the reacting substances, the condition for equilibrium is given by the expression:

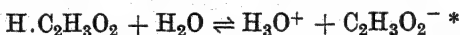
$$\frac{[B_1]^{q_1} \times [B_2]^{q_2} \times [B_3]^{q_3}}{[A_1]^{p_1} \times [A_2]^{p_2} \times [A_3]^{p_3}} = K$$

Expressing this in words, it may be stated: When equilibrium is reached in a reversible reaction, at constant temperature,

the product of the molecular concentrations of the resultants (the substances on the right-hand side of the equation), divided by the product of the molecular concentrations of the reactants (the substances on the left-hand side of the equation), each concentration being raised to a power equal to the number of molecules of that substance taking part in the reaction, is constant.

**I, 10. Application of the Law of Mass Action to Solutions of Electrolytes.**—Attention has already been directed to the fact that weak electrolytes, such as acetic acid and “ammonium hydroxide,” undergo reversible dissociation when dissolved in water. The equilibrium between the undissociated molecules and the ions for such electrolytes can be investigated by means of the law of mass action. The law cannot be applied to strong electrolytes, such as salts, where dissociation is complete, since there is little or no equilibrium between the ions and the undissociated molecules in solution.

The following equilibrium exists in a dilute aqueous solution of acetic acid:



Applying the law of mass action, we have for the equilibrium constant  $K_{\text{equil.}}$ :

$$[\text{C}_2\text{H}_3\text{O}_2^-] \times [\text{H}_3\text{O}^+] / [\text{H.C}_2\text{H}_3\text{O}_2] \times [\text{H}_2\text{O}] = K_{\text{equil.}}$$

The concentration of water  $[\text{H}_2\text{O}]$  is so large as to remain essentially constant, hence we may write:

$$[\text{C}_2\text{H}_3\text{O}_2^-] \times [\text{H}_3\text{O}^+] / [\text{H.C}_2\text{H}_3\text{O}_2] = [\text{H}_2\text{O}] \times K_{\text{equil.}} = K_a,$$

where  $K_a$  is the dissociation or ionisation constant at constant temperature. The term affinity constant is sometimes employed for acids and bases. If 1 gram equivalent of the electrolyte is dissolved in  $V$  litres of solution ( $V = 1/c$ , where  $c$  is the concentration in gram equivalents per litre), and if  $\alpha$  is the degree of dissociation at equilibrium, then the amount of undissociated electrolyte will be  $(1 - \alpha)$  gram equivalents, and the amount of each of the ions will be  $\alpha$  gram equivalents. The

\* The equilibrium was formerly written:



This leads to the same result for the dissociation constant, and here  $\text{H}^+$  is understood to be the solvated proton or hydroxonium ion. This form of the equilibrium equation will be used frequently throughout the text for the sake of simplicity: it should, however, be interpreted in the Brönsted-Lowry sense as explained for acetic acid.

concentration (gram equivalents per litre) of undissociated acetic acid will therefore be  $(1 - \alpha)/V$ , and the concentrations of each of the ions  $\alpha/V$ . Substituting in the equilibrium equation, one obtains the expression:

$$\alpha^2/(1 - \alpha)V = K_a \quad \{\text{or } \alpha^2c/(1 - \alpha) = K_a\}$$

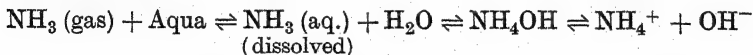
This is known as "Ostwald's dilution law." The agreement of the "law" with experiment is illustrated by the following results for acetic acid at 25°C (Table I, 10, 1).

TABLE I, 10, 1. EQUIVALENT CONDUCTANCE AND DISSOCIATION CONSTANT OF ACETIC ACID AT 25°C

Concn. $\times 10^4$	$\Lambda_e$	$\alpha$	$K_a \times 10^5$
1.873	102.5	0.264	1.78
5.160	65.95	0.170	1.76
9.400	50.60	0.130	1.83
24.78	31.94	0.080	1.82
38.86	25.78	0.066	1.83
56.74	21.48	0.055	1.84
68.71	19.58	0.050	1.84
92.16	16.99	0.044	1.84
112.2	15.41	0.040	1.84
0	388.6		

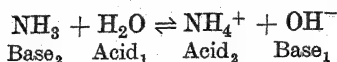
The mean classical or Ostwald dissociation constant of acetic acid at 25° is  $1.82 \times 10^{-5}$ . Similar results—the individual variations may sometimes be slightly greater—are obtained for other weak electrolytes.

The equilibrium in an aqueous solution of a weak base, *e.g.* ammonia, may be discussed in a similar manner. According to classical theory, the series of equilibria may be written:



The term *aqua* denotes solvent water as distinguished from water reacting chemically: the hypothetical ammonium hydroxide was introduced in order to conform with the Arrhenius definition of a base. The vapour pressure of  $\text{NH}_3$  above even dilute solutions of ammonia indicates that the  $\text{NH}_3$  remains largely in the form of dissolved gas. There appears to be little direct evidence for the existence of  $\text{NH}_4\text{OH}$  molecules. Indeed, from the Lowry-Brønsted standpoint, there is little need to

postulate the existence of  $\text{NH}_4\text{OH}$  as the ions can be produced directly by a protolytic reaction between ammonia and water:



The expression for the (concentration) equilibrium constant is:

$$[\text{NH}_4^+] \times [\text{OH}^-] / [\text{NH}_3] = [\text{H}_2\text{O}] \times K_{\text{equil.}} = K_b$$

Since  $[\text{H}_2\text{O}]$  is large and may be considered constant, a new constant  $K_b$ , the **basic dissociation constant** may be employed. Some results for  $K_b$  (due to Ostwald, 1887) for ammonia at  $25^\circ$  are collected in Table I, 10, 2. It may be noted that, in general, for bases  $\text{RNH}_2$ , the same numerical result is obtained if the hypothetical solvated base  $\text{RNH}_2\text{H} \cdot \text{OH}$  is employed in the calculations.

TABLE I, 10, 2. EQUIVALENT CONDUCTANCE AND DISSOCIATION CONSTANT OF AMMONIA AT  $25^\circ$

Dilution (litres)	$\Lambda$	$100\alpha$	$K_b \times 10^5$
8	3.4	1.35	2.3
16	4.8	1.91	2.3
32	6.7	2.66	2.3
64	9.5	3.77	2.3
128	13.5	5.36	2.4
256	19.0	7.54	2.4
$\infty$	252		

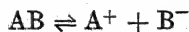
**I, 11. Activity and Activity Coefficient.**—In our deduction of the law of mass action, it was assumed that the effective concentrations or active masses of the components could be expressed by the stoichiometric concentrations. In solutions of electrolytes, this is not the case. Owing to the electrical forces acting between oppositely charged ions, the activity of the ions is reduced, and hence the ions behave as if they were of lower concentration than that calculated from the stoichiometric concentration of the dissolved electrolyte. If, therefore, the law of chemical equilibrium is to be applied to a reaction involving ions, each concentration must be multiplied by a factor which will allow for the interionic attraction. This factor is termed the **activity coefficient** because it gives the fraction of the total concentration which is effective in equilibrium reactions. If we represent the corrected concentration

or activity by  $a$ , the activity coefficient by  $f$  and the concentration by  $c$ , then

$$a = c \times f$$

The value of the activity approaches that of the molar concentration or molarity as the solution is progressively diluted, since under these conditions the ions will be further apart and the interionic attraction will consequently become smaller. At infinite dilution the forces between the ions will be practically zero —  $a = c$  and  $f = 1$ .

The concept of activity, a thermodynamic quantity, was introduced by G. N. Lewis. According to modern thermodynamics, the rigid equilibrium equation for, say, a binary electrolyte:



is

$$a_{A^+} \times a_{B^-} / a_{AB} = K_{therm.}$$

where  $a_{A^+}$ ,  $a_{B^-}$  and  $a_{AB}$  denote the activities of  $A^+$ ,  $B^-$  and  $AB$  respectively, and  $K_{therm.}$  is the **true** or **thermodynamic dissociation constant**. At any molar concentration

$$a_{A^+} = f_{A^+} \cdot [A^+], a_{B^-} = f_{B^-} \cdot [B^-] \text{ and } a_{AB} = f_{AB} \cdot [AB],$$

where  $f$  refers to the activity coefficients, and the square brackets to the molar concentrations. Substituting in the above equation, one obtains:

$$\frac{f_{A^+} \cdot [A^+] \times f_{B^-} \cdot [B^-]}{f_{AB} \cdot [AB]} = \frac{[A^+] \cdot [B^-]}{[AB]} \times \frac{f_{A^+} \times f_{B^-}}{f_{AB}} = K_{therm.}$$

This is the rigorously correct expression for the law of mass action as applied to weak electrolytes.

The activity coefficient varies with the concentration. For ions, it varies with the valency, and has the same value for all dilute solutions having the same **ionic strength**, the latter being a measure of the electrical field existing in the solution. The ionic strength, designated by the symbol  $I$ , was introduced by Lewis and Randall in 1921, and is defined as equal to one-half of the sums of the products of the total concentration of each ion multiplied by the square of its valency, or  $I = 1/2 \sum c_i z_i^2$ , where  $c_i$  is the ionic concentration in gram moles per litre of solution. An example will make this clear. The ionic strength of 0.1 molar  $HNO_3$  solution containing 0.2 molar  $Ba(NO_3)_2$  solution is given by:

$$\begin{aligned} 1/2\{0.1 \text{ (for } H^+) + 0.1 \text{ (for } NO_3^-) + 0.2 \times 2^2 \text{ (for } Ba^{++}) \\ + 0.2 \times 2 \text{ (for } NO_3^-)\} = 1/2\{1.4\} = 0.7 \end{aligned}$$

Activity coefficients may be derived *inter alia*, by making appropriate assumptions, from measurements of the e.m.f. of suitably arranged concentration cells and also from freezing-point data for solutions.\* The Debye-Hückel theory of complete dissociation (1923) has provided a theoretical solution of the problem of calculating individual activities of ions in very dilute solution. The expression for the activity coefficient of an ion is:

$$\log f_i = -Az_i^2\sqrt{I}$$

where  $A$  is a constant,  $z_i$  is the valency of the ion and  $I$  is the ionic strength of the solution.  $A$  may be computed from:

$$A = N^2e^3\sqrt{2\pi/1000}/2.303R^{3/2}\epsilon^{3/2}T^{3/2};$$

$N$  is Avogadro's number;  $e$  the electronic charge;  $R$  the gas constant;  $\epsilon$  the dielectric constant (this is usually taken for

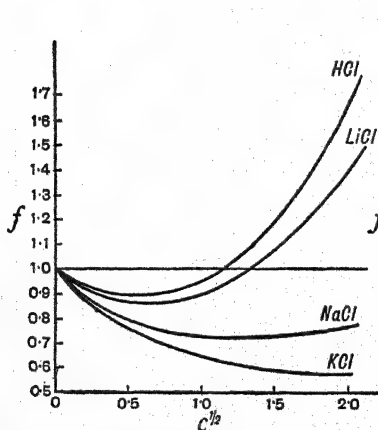


Fig. I, 11, 1

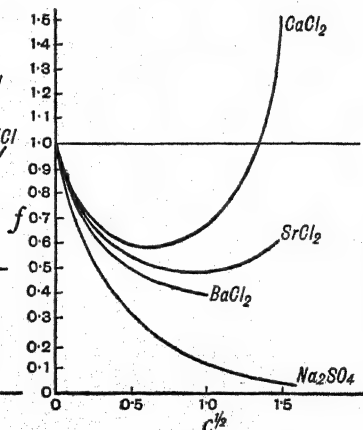


Fig. I, 11, 2

dilute solutions as that of the solvent); and  $T$  is the absolute temperature. The mean activity coefficient of a dilute aqueous solution of a salt at 25° is given by:

$$\log f = -0.509z_+z_-\sqrt{I}$$

where  $z_+$  and  $z_-$  are the valencies of the positive and negative ions respectively. The expression is a limiting one and is applicable to solutions of low ionic strength (up to about  $I = 0.01$ ). The mean activity coefficients (experimental values) of a number of typical electrolytes at round concentra-

\* For details, see, for example, S. Glasstone, *Text Book of Physical Chemistry*, Second Edition, 1947 (Macmillan).



tions are collected in Table I, 11, 1. The activity coefficients, in general, pass through a minimum and then rise gradually; in some cases they exceed the value 1 in the region 1-4 molar. Figs. I, 11, 1 and I, 11, 2 indicate graphically the change in

TABLE I, 11, 1. MEAN ACTIVITY COEFFICIENTS OF VARIOUS ELECTROLYTES

Molar Concentration	0.001	0.01	0.05	0.1	0.2	0.5	1.0	2.0
HCl	0.966	0.904	0.830	0.796	0.767	0.758	0.809	1.01
HBr	0.966	0.906	0.838	0.805	0.782	0.790	0.871	1.17
HNO <sub>3</sub>	0.965	0.902	0.823	0.785	0.748	0.715	0.720	0.78
HIO <sub>3</sub>	0.96	0.86	0.69	0.58	0.46	0.29	0.19	0.10
H <sub>2</sub> SO <sub>4</sub>	0.830	0.544	0.340	0.265	0.209	0.154	0.130	0.12
NaOH	—	—	0.82	—	0.73	0.69	0.68	0.70
KOH	—	0.90	0.82	0.80	—	0.73	0.76	0.89
Ba(OH) <sub>2</sub>	—	0.712	0.526	0.443	0.370	—	—	—
AgNO <sub>3</sub>	—	0.90	0.79	0.72	0.64	0.51	0.40	0.28
Al(NO <sub>3</sub> ) <sub>3</sub>	—	—	—	0.20	0.16	0.14	0.19	0.45
BaCl <sub>2</sub>	0.88	0.72	0.56	0.49	0.44	0.39	0.39	0.44
Ba(NO <sub>3</sub> ) <sub>2</sub>	0.88	0.71	0.52	0.43	0.34	—	—	—
CaCl <sub>2</sub>	0.89	0.73	0.57	0.52	0.48	0.52	0.71	—
Ca(NO <sub>3</sub> ) <sub>2</sub>	0.88	0.71	0.54	0.48	0.42	0.38	0.35	0.35
CdCl <sub>2</sub>	0.76	0.47	0.28	0.21	0.15	0.09	0.06	—
CdSO <sub>4</sub>	0.73	0.40	0.21	0.17	0.11	0.07	0.05	0.04
CuCl <sub>2</sub>	0.89	0.72	0.58	0.52	0.47	0.42	0.43	0.51
CuSO <sub>4</sub>	0.74	0.41	0.21	0.16	0.11	0.07	0.05	—
FeCl <sub>2</sub>	0.89	0.75	0.62	0.58	0.55	0.59	0.67	—
KF	—	0.93	0.88	0.85	0.81	0.74	0.71	0.70
KCl	0.965	0.901	0.815	0.769	0.719	0.651	0.606	0.576
KBr	0.965	0.903	0.822	0.777	0.728	0.665	0.625	0.602
KI	0.965	0.905	0.84	0.80	0.76	0.71	0.68	0.69
KClO <sub>3</sub>	0.967	0.907	0.813	0.755	—	—	—	—
KClO <sub>4</sub>	0.965	0.895	0.788	—	—	—	—	—
K <sub>2</sub> SO <sub>4</sub>	0.89	0.71	0.52	0.43	0.36	—	—	—
K <sub>4</sub> Fe(CN) <sub>6</sub>	—	—	0.19	0.14	0.11	0.67	—	—
LiBr	0.966	0.909	0.842	0.810	0.784	0.783	0.848	1.06
Mg(NO <sub>3</sub> ) <sub>2</sub>	0.88	0.71	0.55	0.51	0.46	0.44	0.50	0.69
MgSO <sub>4</sub>	—	0.40	0.22	0.18	0.13	0.09	0.06	0.05
NH <sub>4</sub> Cl	0.96	0.88	0.79	0.74	0.69	0.62	0.57	—
NH <sub>4</sub> Br	0.96	0.87	0.78	0.73	0.68	0.62	0.57	—
NH <sub>4</sub> I	0.96	0.89	0.80	0.76	0.71	0.65	0.60	—
NH <sub>4</sub> NO <sub>3</sub>	0.96	0.88	0.78	0.73	0.66	0.56	0.47	—
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	0.87	0.67	0.48	0.40	0.32	0.22	0.16	—
NaF	—	0.90	0.81	0.75	0.69	0.62	—	—
NaCl	0.966	0.904	0.823	0.780	0.730	0.68	0.66	0.67
NaBr	0.966	0.914	0.844	0.800	0.740	0.695	0.686	0.734
NaI	0.97	0.91	0.86	0.83	0.81	0.78	0.80	0.95
NaNO <sub>3</sub>	0.966	0.90	0.82	0.77	0.70	0.62	0.55	0.48
Na <sub>2</sub> SO <sub>4</sub>	0.89	0.71	0.53	0.45	0.36	0.27	0.20	—
NaClO <sub>4</sub>	0.97	0.90	0.82	0.77	0.72	0.64	0.58	—
Pb(NO <sub>3</sub> ) <sub>2</sub>	0.88	0.69	0.46	0.37	0.27	0.17	0.11	—
ZnCl <sub>2</sub>	0.88	0.71	0.56	0.50	0.45	0.38	0.33	—
ZnSO <sub>4</sub>	0.70	0.39	—	0.15	0.11	0.07	0.05	0.04

activity coefficient with increasing concentration for a few selected electrolytes:  $f$  is plotted against the square root of the concentration (g. mols. per 1,000 g. of solvent)  $c$ .

The activity coefficients of unionised molecules do not differ appreciably from unity. For weak electrolytes in which the ionic concentration and therefore the ionic strength is small, the error introduced by neglecting the difference between the actual values of the activity coefficients of the ions,  $f_{A^+}$  and  $f_{B^-}$ , and unity is small ( $<5\%$ ). Hence for weak electrolytes, the true or thermodynamic expression reduces to

$$[A^+] \times [B^-]/[AB] = K;$$

the constants obtained by the use of simple concentrations will be accurate to 2–6%. Such values are sufficiently precise for purposes of calculation in qualitative analysis. It must, however, be pointed out that precision values for the dissociation constants of weak electrolytes can be obtained by the use of special methods; the discussion of these is outside the scope of this volume.

For strong electrolytes, as well as for the more concentrated solutions of weak electrolytes, activity coefficients should be employed when precise results are required. Activity coefficients, particularly for solutions containing mixtures of salts of various valence types such as are encountered in qualitative analysis, are difficult to determine. For this reason, we shall employ the molecular concentrations instead of activities in this text. Strong electrolytes will be assumed to be completely dissociated and no correction for activity coefficients will generally be made. Fortunately, in a large number of cases, the errors thus introduced are not very serious.

**I, 12. Strengths of Acids and Bases.**—It has already been stated that the properties of acids are the properties of the hydrogen ion  $H^+$  (or, more correctly, the hydroxonium ion  $H_3O^+$ ). For any given total concentration of acid, the concentration of the hydrogen ions will depend upon the degree of dissociation  $\alpha$ ; the strength of an acid will thus depend upon the value of  $\alpha$  at a given concentration. The dissociation constant gives a relationship between  $\alpha$  and the concentration, and it accordingly also represents a measure of the strength of the acid or a measure of its tendency to undergo dissociation.

The properties of bases, according to the most elementary view,\* depend upon the hydroxyl ion and the ionisation constant will likewise be a measure of the strength of the base.

\* See Section I, 5 for Brönsted-Lowry definition.

TABLE I, 12, 1. DISSOCIATION CONSTANTS AT 25°C

<i>Monobasic Acids</i>			
Nitrous acid	$4.6 \times 10^{-4}$	Monochloroacetic acid	$1.5 \times 10^{-3}$
Hydrocyanic acid	$7.24 \times 10^{-10}$	Cyanoacetic acid	$3.49 \times 10^{-3\dagger}$
Formic acid	$1.77 \times 10^{-4\dagger}$	Phenylacetic acid	$4.88 \times 10^{-5\dagger}$
Acetic acid	$1.82 \times 10^{-5}$	Benzoic acid	$6.37 \times 10^{-5\dagger}$
	$1.76 \times 10^{-5\dagger}$	<i>o</i> -Chlorobenzoic acid	$1.20 \times 10^{-3\dagger}$
Propionic acid	$1.34 \times 10^{-5}$	<i>o</i> -Nitrobenzoic acid	$6.00 \times 10^{-4\dagger}$
Boric acid	$5.8 \times 10^{-10}$	Hydrofluoric acid	$6.9 \times 10^{-4}$
		Phenol	$1.3 \times 10^{-10}$
<i>Dibasic Acids</i>			
Hydrogen sulphide	$\begin{cases} K_1 & 9.1 \times 10^{-8} \\ K_2 & 1.2 \times 10^{-15} \end{cases}$	Oxalic acid	$\begin{cases} K_1 & 5.9 \times 10^{-2\dagger} \\ K_2 & 6.4 \times 10^{-5\dagger} \end{cases}$
Sulphurous acid	$\begin{cases} K_1 & 1.7 \times 10^{-2} \\ K_2 & 1.0 \times 10^{-7} \end{cases}$	Malonic acid	$\begin{cases} K_1 & 1.40 \times 10^{-3\dagger} \\ K_2 & 2.20 \times 10^{-6\dagger} \end{cases}$
Sulphuric acid	$\begin{cases} K_1 & 1.15 \times 10^{-2\dagger} \\ K_2 & 4.31 \times 10^{-7\dagger} \end{cases}$	Succinic acid	$\begin{cases} K_1 & 6.63 \times 10^{-5\dagger} \\ K_2 & 2.54 \times 10^{-6\dagger} \end{cases}$
Carbonic acid	$\begin{cases} K_1 & 4.31 \times 10^{-7\dagger} \\ K_2 & 5.61 \times 10^{-11\dagger} \end{cases}$	<i>d</i> -Tartaric acid	$\begin{cases} K_1 & 1.04 \times 10^{-3\dagger} \\ K_2 & 4.55 \times 10^{-4\dagger} \end{cases}$
<i>Tribasic Acids</i>			
Phosphoric acid	$\begin{cases} K_1 & 7.52 \times 10^{-3\dagger} \\ K_2 & 6.23 \times 10^{-8\dagger} \\ K_3 & 5 \times 10^{-13\dagger} \end{cases}$	Citric acid	$\begin{cases} K_1 & 9.20 \times 10^{-4\dagger} \\ K_2 & 2.69 \times 10^{-5\dagger} \\ K_3 & 1.34 \times 10^{-6\dagger} \end{cases}$
Arsenic acid	$\begin{cases} K_1 & 5.0 \times 10^{-3} \\ K_2 & 4.0 \times 10^{-5} \\ K_3 & 6.0 \times 10^{-10} \end{cases}$		
<i>Bases</i>			
Ammonia	$1.8 \times 10^{-5}$	Diethylamine	$1.2 \times 10^{-3}$
	$1.79 \times 10^{-5\dagger}$	Triethylamine	$6.4 \times 10^{-4}$
Methylamine	$4.38 \times 10^{-4\dagger}$	Aniline	$4.0 \times 10^{-10}$
Dimethylamine	$5.20 \times 10^{-5\dagger}$	Pyridine	$2.0 \times 10^{-9}$
Trimethylamine	$5.45 \times 10^{-5\dagger}$	Quinoline	$6.0 \times 10^{-10}$
Ethylamine	$5.6 \times 10^{-4}$	Piperidine	$1.3 \times 10^{-3}$

† Figures marked with a dagger (†) are the true or thermodynamic dissociation constants (see Section I, 11).

For very weak or slightly dissociated electrolytes, the expression  $\alpha^2/(1 - \alpha)V = K$  reduces to  $\alpha^2 = KV$  or  $\alpha = \sqrt{KV}$ , since  $\alpha$  may be neglected in comparison with unity. Hence for any two weak acids or bases at any given dilution  $V$  (in litres), one has  $\alpha_1 = \sqrt{K_1V}$  and  $\alpha_2 = \sqrt{K_2V}$ , or  $\alpha_1/\alpha_2 = \sqrt{K_1}/\sqrt{K_2}$ . Expressed in words, for any two weak or slightly dissociated electrolytes at equal dilutions, the degrees of dissociation are proportional to the square roots of their dissociation constants. Some values for the dissociation constants at  $25^\circ$  for weak acids and bases are collected in Table I, 12, 1.

**I, 13. Dissociation of Polybasic Acids.**—When a polybasic acid is dissolved in water, the various hydrogen atoms undergo dissociation to different extents. For a dibasic acid  $H_2A$ , the primary and secondary dissociation can be represented by the equations:



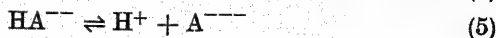
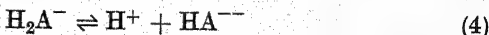
If the dibasic acid is a weak electrolyte, the law of mass action may be applied, and the following expressions obtained:

$$[H^+] \times [HA^-]/[H_2A] = K_1 \quad (1a)$$

$$[H^+] \times [A^{--}]/[HA^-] = K_2 \quad (2a)$$

$K_1$  and  $K_2$  are known as the **primary** and **secondary dissociation constants** respectively. Each stage of the dissociation process has its own ionisation constant, and the magnitudes of these constants give a measure of the extent to which each ionisation has proceeded at any given concentration. The greater the value of  $K_1$  relative to  $K_2$ , the smaller will be the secondary dissociation, and the greater must be the dilution before the latter becomes appreciable. It is therefore possible that a dibasic (or polybasic) acid may behave, so far as dissociation is concerned, as a monobasic acid over a considerable concentration range. This is indeed characteristic of many polybasic acids (see Table I, 12, 1).

A **tribasic acid**  $H_3A$  (e.g. orthophosphoric acid) will similarly yield three dissociation constants,  $K_1$ ,  $K_2$  and  $K_3$ , which may be computed in an analogous manner:



We can now apply some of the theoretical considerations to actual examples encountered in qualitative analysis.\*

*Example 1.* To calculate the concentrations of  $\text{HS}^-$  and  $\text{S}^{--}$  in a saturated solution of hydrogen sulphide.

A saturated aqueous solution of hydrogen sulphide at  $25^\circ$ , at atmospheric pressure, is approximately 0.1 molar. The primary and secondary dissociation constants are  $9.1 \times 10^{-8}$  and  $1.2 \times 10^{-15}$  respectively.

$$\text{Thus} \quad [\text{H}^+] \times [\text{HS}^-]/[\text{H}_2\text{S}] = 9.1 \times 10^{-8} \quad (\text{i})$$

$$\text{and} \quad [\text{H}^+] \times [\text{S}^{--}]/[\text{HS}^-] = 1.2 \times 10^{-15} \quad (\text{ii})$$

The very much smaller value of  $K_2$  indicates that the secondary dissociation, and consequently  $[\text{S}^{--}]$  is exceedingly small. It follows, therefore, that only the primary ionisation is of importance, and  $[\text{H}^+]$  and  $[\text{HS}^-]$  are practically equal in value. Substituting in equation (i):  $[\text{H}^+] = [\text{HS}^-]$  and  $[\text{H}_2\text{S}] = 0.1$ , one obtains  $[\text{H}^+] = [\text{HS}^-] = \sqrt{9.1 \times 10^{-8} \times 0.1} = 9.5 \times 10^{-5}$ .

Both the equilibrium equations must be satisfied simultaneously; by substitution of these values for  $[\text{H}^+]$  and  $[\text{HS}^-]$  in equation (ii) one obtains  $9.5 \times 10^{-5} \times [\text{S}^{--}] = 1.2 \times 10^{-15} \times 9.5 \times 10^{-5}$ , or  $[\text{S}^{--}] = 1.2 \times 10^{-15}$ , which is the value for  $K_2$ .

If one multiplies equations (i) and (ii) together and transposes:

$$[\text{S}^{--}] = 1.1 \times 10^{-23}/[\text{H}^+]^2$$

Thus the concentration of the sulphide ion is inversely proportional to the square of the hydrogen ion concentration, *i.e.* if one, say, doubles  $[\text{H}^+]$  by the addition of a strong acid, the  $[\text{S}^{--}]$  would be reduced to  $1/2^2$  or  $1/4$  of its original value.

**I, 14. Common Ion Effect.**—The concentration of a particular ion in an ionic reaction can be increased by the addition of a compound which produces that ion upon dissociation. The particular ion is thus derived from the compound already in solution and from the added reagent, hence the name **common ion**. We shall confine our attention to the case in which the original compound is a weak electrolyte in order that the law of mass action may be applicable. The result is usually that there is a higher concentration of this ion in solution than that derived from the original compound alone, and new equilibrium conditions will be produced. Examples of the calculation of the common ion effect are given below. In general, it may be stated that if the total concentration of the common ion is only slightly larger than that which the original compound alone would furnish, the effect is small; if, however, the

\* For further examples the reader is referred to any of the numerous books on chemical calculations.

concentration of the common ion is very much increased (e.g. that produced by the addition of a completely dissociated salt), the effect is very great and may be of considerable practical importance. Indeed, the common ion effect provides a valuable method for controlling the concentration of the ions furnished by a weak electrolyte.

*Example 2.* To calculate the sulphide ion concentration in a 0.25 molar hydrochloric acid solution saturated with hydrogen sulphide.

This concentration has been chosen since it is that at which the sulphides of the metals of Group II are precipitated. The total concentration of hydrogen sulphide will be approximately the same as in aqueous solution, i.e. 0.1M; the  $[H^+]$  will be equal to that of the completely dissociated HCl, i.e. 0.25M, but the  $[S^{--}]$  will be reduced below  $1.2 \times 10^{-15}$ .

Substituting in equations (i) and (ii) (Section I, 13), one finds:

$$[HS^-] = \frac{9.1 \times 10^{-8} \times [H_2S]}{[H^+]} = \frac{9.1 \times 10^{-8} \times 0.1}{0.25} = 3.6 \times 10^{-8},$$

$$[S^{--}] = \frac{1.2 \times 10^{-15} \times [HS^-]}{[H^+]} = \frac{1.2 \times 10^{-15} \times 3.6 \times 10^{-8}}{0.25}$$

$$= 1.7 \times 10^{-22}$$

Thus by changing the acidity from  $9.5 \times 10^{-5}M$  (that present in saturated  $H_2S$  water) to 0.25M, the sulphide ion concentration is reduced from  $1.2 \times 10^{-15}$  to  $1.7 \times 10^{-22}$ .

*Example 3.* What effect has the addition of 0.1 gram molecule (8.20 grams) of anhydrous sodium acetate to 1 litre of 0.1 molar acetic acid upon the degree of ionisation of the acid?

The dissociation constant of acetic acid at 25° is  $1.82 \times 10^{-5}$ . The degree of dissociation  $\alpha$  in 0.1M solution ( $c = 0.1$ ) may be computed by solving the quadratic equation:

$$\frac{[H^+] \times [C_2H_3O_2^-]}{[H.C_2H_3O_2]} = \frac{\alpha^2 c}{(1 - \alpha)} = 1.82 \times 10^{-5}$$

For our purpose it is sufficiently accurate to neglect  $\alpha$  in  $(1 - \alpha)$ , since  $\alpha$  is small:

$$\therefore \alpha = \sqrt{K/c} = \sqrt{1.82 \times 10^{-4}} = 0.0135$$

Hence in 0.1M acetic acid,

$$[H^+] = 0.00135, [C_2H_3O_2^-] = 0.00135 \text{ and } [H.C_2H_3O_2] = 0.0986.$$

The concentrations of sodium and acetate ions produced by the addition of the completely dissociated sodium acetate are:

$$[Na^+] = 0.1 \text{ and } [C_2H_3O_2^-] = 0.1 \text{ gram mole respectively.}$$

The acetate ions from the salt will tend to decrease the ionisation of the acetic acid since  $K$  is constant, and consequently the acetate ion

concentration derived from it. Hence we may write,  $[C_2H_3O_2^-] = 0.1$  for the solution, if  $\alpha'$  is the new degree of ionisation,

$$[H^+] = \alpha'c = 0.1\alpha' \quad \text{and} \quad [H.C_2H_3O_2] = (1 - \alpha')c = 0.1,$$

since  $\alpha'$  is negligibly small.

Substituting in the mass action equation:

$$\frac{[H^+] \times [C_2H_3O_2^-]}{[H.C_2H_3O_2]} = \frac{0.1\alpha' \times 0.1}{0.1} = 1.82 \times 10^{-5},$$

$$\text{or} \quad \alpha' = 1.8 \times 10^{-4}$$

$$[H^+] = \alpha'c = 1.8 \times 10^{-5}$$

The addition of a tenth of an equivalent weight of sodium acetate to a 0.1 molar solution of acetic acid has decreased the degree of ionisation from 1.35 to 0.018 per cent, and the hydrogen ion concentration from 0.0135 to 0.000018.

*Example 4.* What effect has the addition of 0.5 gram molecule (26.75 grams) of ammonium chloride to one litre of 0.1 molar ammonia solution upon the degree of dissociation of the base?

(Dissociation constant of  $NH_3 = 1.8 \times 10^{-5}$ )

In 0.1M ammonia solution  $\alpha = \sqrt{1.8 \times 10^{-5} / 0.1} = 0.013$ . Hence  $[OH^-] = 0.0013$ ,  $[NH_4^+] = 0.0013$  and  $[NH_3] = 0.0987$ . Let  $\alpha'$  be the degree of dissociation in the presence of the added ammonium chloride. Then  $[OH^-] = \alpha'c = 0.1\alpha'$  and  $[NH_3] = (1 - \alpha')c = 0.1$ , since  $\alpha'$  may be taken as negligibly small. The addition of the completely ionised ammonium chloride will of necessity decrease the  $[NH_4^+]$  derived from the base and increase  $[NH_3]$ , since  $K$  is constant under all conditions. Now  $[NH_4^+] = 0.5$ , as a first approximation.

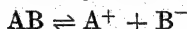
Substituting in the equation:

$$\frac{[NH_4^+] \times [OH^-]}{[NH_3]} = \frac{0.5 \times 0.1\alpha'}{0.1} = 1.8 \times 10^{-5},$$

$$\text{or} \quad \alpha' = 3.6 \times 10^{-5} \quad \text{and} \quad [OH^-] = 3.6 \times 10^{-6}$$

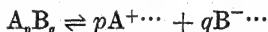
The addition of half of an equivalent weight of ammonium chloride to a 0.1 molar solution of ammonia has decreased the degree of ionisation from 1.35 to 0.0036 per cent, and the hydroxyl ion concentration from 0.0013 to 0.0000036.

**I, 15. Solubility Product.**—It was found as a result of experiment that for sparingly soluble binary electrolytes (*i.e.* those with solubilities less than 0.001 gram molecules per litre), the product of the total molar concentrations of the ions is constant at constant temperature. This product  $S^c$  is termed the solubility product. For a binary electrolyte:



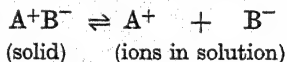
$$S_{AB}^c = [A^+] \times [B^-]$$

Nernst, about 1889, enunciated the **solubility product principle** in the form: in a saturated solution of a sparingly soluble electrolyte, the product of the concentrations of the constituent ions for any given temperature is constant, the ion concentration being raised to powers equal to the respective numbers of ions of each kind furnished by the dissociation of one molecule of the electrolyte. (The concentration of an ion may be changed by adding another electrolyte yielding an ion in common with the solid substance, but the solubility product remains the same: if, say, for a binary electrolyte, the concentration of one ion increases, that of the other ion decreases correspondingly.) Thus for an electrolyte  $A_pB_q$ , which ionises into  $pA^{+...}$  and  $qB^{-...}$  ions:



$$S_{ApB}^s = [A^{+...}]^p \times [B^{-...}]^q$$

This relationship can be derived as follows. For simplicity, let us consider a saturated solution of a slightly soluble binary electrolyte in which excess of solid is present:



The activities of the solid and the ions in solution may be written as  $a_{AB}$ ,  $a_{A^+}$  and  $a_{B^-}$  respectively. The solid is completely ionised in dilute solution. By applying the law of mass action in its most general form, we have:

$$a_{A^+} \times a_{B^-} / a_{AB} = K_{\text{equil.}}$$

The activity of the solid may be taken as unity since it is the pure component. Its ability to lose ions to a solution may depend upon the extent of its surface in contact with the solution, but the tendency of the ions to crystallise out also depends upon the nature of this same surface and hence, as far as equilibrium is concerned, the surface factor cancels out. The amount of solid present has no effect upon the equilibrium provided a reasonable quantity is present. The expression for the equilibrium constant therefore reduces to:

$$a_{A^+} \times a_{B^-} = S_{AB}^s$$

where  $S_{AB}^s$  is the **activity product constant**. Now activity = concentration  $\times$  activity coefficient, hence:

$$[A^+] \cdot f_{A^+} \times [B^-] \cdot f_{B^-} = S_{AB}^s$$



In very dilute solutions of the sparingly soluble salt, the activity coefficients are close to unity and we may then write:

$$[A^+] \times [B^-] = S_{AB}$$

It is important to note that the solubility product relation applies only to saturated solutions of slightly soluble electrolytes and with *small* additions of other salts, say, provided the total salt concentration does not exceed 0.2–0.3 molar. In the presence of large concentrations of salts, the ionic concentration and therefore the ionic strength of the solution will increase. This will, in general, lower the activity coefficients of both ions (since  $\log f_i = -Az_i^2\sqrt{I}$ , Section I, 11). As a consequence the solubility of the slightly soluble salt must increase since

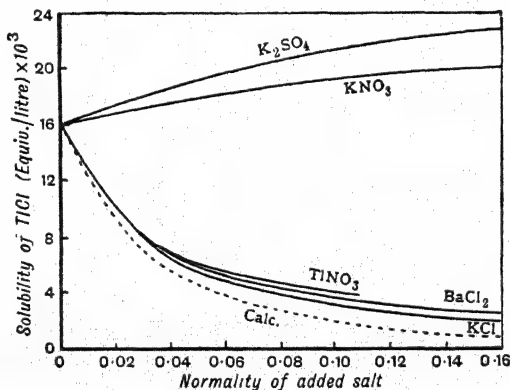


Fig. 1, 15, 1.—Influence of Various Salts on the Solubility of TiCl

$[A^+] \times [B^-] \cdot f_{A^+} \times f_{B^-}$  must be kept constant. The effect of electrolytes with no common ion upon the solubility is often called the *salt effect*. The salt effect is illustrated by the curves shown in Figs. 1, 15, 1 and 1, 15, 2. In the former the three salts with the common ion decrease the solubility of TiCl somewhat less than the solubility product predicts, whilst the two salts with no common ion increase the solubility, the divalent sulphate ion exerting the greater effect. In the latter case excess of AgNO<sub>3</sub> decreases the solubility somewhat less than simple theory predicts, MgSO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub> decrease the solubility only slightly, whilst KNO<sub>3</sub> and Mg(NO<sub>3</sub>)<sub>2</sub> markedly increase the solubility with the divalent magnesium ion causing the greater increase. These effects, which are inexplicable on the basis of the classical theory of Arrhenius, can be readily

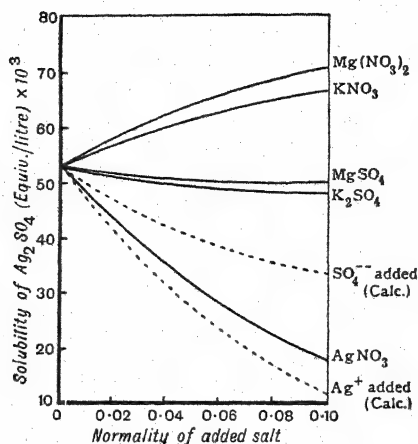


Fig. 1, 15, 2.—Influence of Various Salts on the Solubility of  $\text{Ag}_2\text{SO}_4$

understood on the basis of the influence of the various salts upon the activity coefficients. It will be observed that whilst the influence of a salt with a common ion is to depress the solubility (the dotted curve indicates the solubility calculated from the simple solubility product relationship), this decrease is often greatly modified by the salt effect: indeed, with  $\text{MgSO}_4$  the salt effect nearly cancels out the common ion effect.

The great importance of the conception of solubility product lies in its bearing upon precipitation from solution, which is, of course, one of the principal operations of qualitative analysis. The solubility product is the ultimate value which is attained by the ionic product when equilibrium has been established between the solid phase of a difficultly soluble salt and the solution. If the experimental conditions are such that the ionic product is different from the solubility product, then the system will attempt to adjust itself in such a manner that the ionic and solubility products are equal in value. Thus, if, for a given electrolyte, the product of the concentrations of the ions in solution is arbitrarily made to exceed the solubility product, as for example by the addition of a salt with a common ion, the adjustment of the system results in the precipitation of the solid salt, provided supersaturation conditions are excluded. If the ionic product is less than the solubility product or can arbitrarily be made smaller, as for example by complex salt formation or by the formation of weak electro-

lytes (see Section I, 20), then a further quantity of the solute can pass into solution until the solubility product is attained, or if this is not possible, until all the solute has dissolved.

The concentrations are expressed in gram moles per litre for the calculation of solubility products. A few examples may help the student to understand the subject fully.

*Example 5.* The solubility of silver chloride is 0.0015 grams per litre. Calculate the solubility product.

The molecular weight of AgCl is 143.5.

The solubility is therefore  $0.0015/143.5 = 1.05 \times 10^{-5}$  moles per litre. In a saturated solution the dissociation,  $\text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$ , is complete; 1 mole of AgCl will give 1 mole each of  $\text{Ag}^+$  and  $\text{Cl}^-$ .

Hence  $[\text{Ag}^+] = 1.05 \times 10^{-5}$  and  $[\text{Cl}^-] = 1.05 \times 10^{-5}$

$$S_{\text{AgCl}} = [\text{Ag}^+] \times [\text{Cl}^-] = (1.05 \times 10^{-5}) \times (1.05 \times 10^{-5}) \\ = 1.1 \times 10^{-10}$$

*Example 6.* Calculate the solubility product of silver chromate, given that its solubility is  $2.5 \times 10^{-2}$  grams per litre.



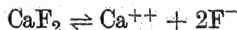
The molecular weight of  $\text{Ag}_2\text{CrO}_4$  is 332, hence the solubility  $= 2.5 \times 10^{-2}/332 = 7.5 \times 10^{-5}$  mole per litre.

Now 1 mole of  $\text{Ag}_2\text{CrO}_4$  gives two moles of  $\text{Ag}^+$  and 1 mole of  $\text{CrO}_4^{--}$ , therefore

$$S_{\text{Ag}_2\text{CrO}_4} = [\text{Ag}^+]^2 \times [\text{CrO}_4^{--}] \\ = (2 \times 7.5 \times 10^{-5})^2 \times (7.5 \times 10^{-5}) \\ = 1.7 \times 10^{-12}$$

*Example 7.* The concentration of fluoride ion in a saturated aqueous solution of  $\text{CaF}_2$  is 0.0078 gram per litre. Calculate the solubility product of calcium fluoride.

The dissociation can be written:

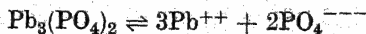


i.e. in a saturated aqueous solution the concentration of  $\text{Ca}^{++}$  is half that of  $\text{F}^-$ . The fluoride ion concentration is  $0.0078/19 = 4.0 \times 10^{-4}$  mole per litre, and the calcium ion concentration is therefore  $2.0 \times 10^{-4}$  mole per litre.

$$S_{\text{CaF}_2} = [\text{Ca}^{++}] \times [\text{F}^-]^2 = (2.0 \times 10^{-4}) \times (4.0 \times 10^{-4})^2 \\ = 3.2 \times 10^{-11}$$

*Example 8.* The solubility product of lead orthophosphate is  $1.5 \times 10^{-32}$ . Calculate the solubility in grams per litre.

The dissociation is:



If  $x$  is the solubility in gram moles per litre,  $[\text{Pb}^{++}] = 3x$  and  $[\text{PO}_4^{---}] = 2x$ .

$$S_{\text{Pb}_3(\text{PO}_4)_2} = [\text{Pb}^{++}]^3 \times [\text{PO}_4^{---}]^2$$

$$\text{or } 1.5 \times 10^{-32} = (3x)^3 \times (2x)^2$$

$$\text{or } x^5 = 1.5 \times 10^{-32}/108$$

$$\text{or } x = \sqrt[5]{13.9 \times 10^{-35}} = 1.70 \times 10^{-7} \text{ mole per litre}$$

The molecular weight of  $\text{Pb}_3(\text{PO}_4)_2$  is 358, hence the solubility is

$$1.70 \times 10^{-7} \times 358 = 6.1 \times 10^{-5} \text{ grams per litre}$$

*Example 9.* Given that the solubility product of magnesium hydroxide is  $3.4 \times 10^{-11}$ , calculate the concentration of hydroxide ions in a saturated aqueous solution.



If  $2x$  is the concentration of  $\text{OH}^-$  in gram molecules per litre, then  $[\text{Mg}^{++}] = x$ .

$$S_{\text{Mg}(\text{OH})_2} = [\text{Mg}^{++}] \times [\text{OH}^-]^2$$

$$\text{or } 3.4 \times 10^{-11} = x \times (2x)^2$$

$$\text{or } x^3 = 3.4 \times 10^{-11}/4$$

$$\text{or } x = \sqrt[3]{8.5 \times 10^{-12}} = 2.04 \times 10^{-4} \text{ gram mole per litre}$$

$$\text{or } [\text{OH}^-] = 2x = 4.08 \times 10^{-4} \text{ gram mole per litre}$$

In order to explain many of the reactions of qualitative analysis in a clear and intelligent manner, the values of the solubility products of the various sparingly soluble substances are useful. Some of the most important figures are collected in Table I, 15, 1, and what appear to be most trustworthy values in the literature are given. The student is referred to text-books on physical chemistry for a description of the methods for determining these quantities. Many of these constants are obtained by indirect means, such as measurements of electrical conductivity, of e.m.f. of cells, or from thermodynamic calculations using thermal data. The various methods, however, do not always give consistent results and this may be attributed to various causes, which include the following. In some cases the physical structure, and hence the solubility of the precipitate at the time of precipitation, is not the same as that of an old or stabilised precipitate: this may be due to the process known as "ripening", which is a sort of recrystallisation, or it may be due to a real change of crystal structure. Thus for nickel sulphide three forms ( $\alpha$ ,  $\beta$  and  $\gamma$ ) have been reported with solubility products of  $3 \times 10^{-21}$ ,  $1 \times 10^{-26}$  and  $2 \times 10^{-23}$  respectively: another source gives one

value of  $1.4 \times 10^{-24}$ . The  $\alpha$ -form is said to be that of the freshly precipitated substance: the other forms are produced on standing. For cadmium sulphide a value of  $1.4 \times 10^{-28}$  has been computed from thermal and other data (Latimer, 1938), whilst direct determination leads to a solubility product of  $5.5 \times 10^{-25}$  (Belcher, 1949).

TABLE I, 15, 1. SOLUBILITY PRODUCTS AT THE LABORATORY TEMPERATURE

<i>Substance</i>	<i>Solubility product</i>	<i>Substance</i>	<i>Solubility product</i>
AgBr	$7.7 \times 10^{-13}$	FeS	$4.0 \times 10^{-19}$
AgBrO <sub>3</sub>	$5.0 \times 10^{-5}$	Hg <sub>2</sub> Br <sub>2</sub>	$5.2 \times 10^{-23}$
AgCNS	$1.2 \times 10^{-12}$	Hg <sub>2</sub> Cl <sub>2</sub>	$3.5 \times 10^{-18}$
AgCl	$1.5 \times 10^{-10}$	Hg <sub>2</sub> I <sub>2</sub>	$1.2 \times 10^{-28}$
Ag <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	$5.0 \times 10^{-12}$	Hg <sub>2</sub> S	$1 \times 10^{-45}$ ✓
Ag <sub>2</sub> CrO <sub>4</sub>	$2.4 \times 10^{-12}$	HgS	$4 \times 10^{-54}$
AgI	$0.9 \times 10^{-16}$	K <sub>2</sub> [PtCl <sub>6</sub> ]	$1.1 \times 10^{-5}$
AgIO <sub>3</sub>	$2.0 \times 10^{-8}$	MgCO <sub>3</sub>	$1.0 \times 10^{-5}$
Ag <sub>3</sub> PO <sub>4</sub>	$1.8 \times 10^{-18}$	MgC <sub>2</sub> O <sub>4</sub>	$8.6 \times 10^{-5}$
Ag <sub>2</sub> S	$1.6 \times 10^{-49}$	MgF <sub>2</sub>	$7.0 \times 10^{-9}$
Ag <sub>2</sub> SO <sub>4</sub>	$7.7 \times 10^{-5}$	Mg(NH <sub>4</sub> )PO <sub>4</sub>	$2.5 \times 10^{-13}$
Al(OH) <sub>3</sub>	$8.5 \times 10^{-23}$	Mg(OH) <sub>2</sub>	$3.4 \times 10^{-11}$
BaCO <sub>3</sub>	$8.1 \times 10^{-9}$	Mn(OH) <sub>2</sub>	$4.0 \times 10^{-14}$
BaC <sub>2</sub> O <sub>4</sub>	$1.7 \times 10^{-7}$	MnS	$1.4 \times 10^{-15}$
BaCrO <sub>4</sub>	$1.6 \times 10^{-10}$	Ni(OH) <sub>2</sub>	$8.7 \times 10^{-19}$
BaSO <sub>4</sub>	$9.2 \times 10^{-11}$	NiS	$1.4 \times 10^{-24}$
Bi <sub>2</sub> S <sub>3</sub>	$1.6 \times 10^{-72}$	PbBr <sub>2</sub>	$7.9 \times 10^{-5}$
CaCO <sub>3</sub>	$4.8 \times 10^{-9}$	PbCl <sub>2</sub>	$2.4 \times 10^{-4}$
CaC <sub>2</sub> O <sub>4</sub>	$2.6 \times 10^{-9}$	PbCO <sub>3</sub>	$3.3 \times 10^{-14}$
CaF <sub>2</sub>	$3.2 \times 10^{-11}$	PbCrO <sub>4</sub>	$1.8 \times 10^{-14}$
CaSO <sub>4</sub>	$2.3 \times 10^{-4}$	PbF <sub>2</sub>	$3.7 \times 10^{-8}$
CdS	$1.4 \times 10^{-28}$	PbI <sub>2</sub>	$8.7 \times 10^{-9}$
Co(OH) <sub>2</sub>	$1.6 \times 10^{-18}$	Pb <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	$1.5 \times 10^{-32}$
Co(OH) <sub>3</sub>	$2.5 \times 10^{-43}$	PbS	$5 \times 10^{-29}$
CoS	$3 \times 10^{-26}$	PbSO <sub>4</sub>	$2.2 \times 10^{-8}$
Cr(OH) <sub>3</sub>	$2.9 \times 10^{-29}$	SrCO <sub>3</sub>	$1.6 \times 10^{-9}$
CuBr	$1.6 \times 10^{-11}$	SrC <sub>2</sub> O <sub>4</sub>	$5.0 \times 10^{-8}$
CuCl	$1.0 \times 10^{-6}$	SrSO <sub>4</sub>	$2.8 \times 10^{-7}$
CuI	$5.0 \times 10^{-12}$	TiCl	$1.5 \times 10^{-4}$
CuS	$1 \times 10^{-44}$	TH	$2.8 \times 10^{-8}$
CuSCN	$1.6 \times 10^{-11}$	Tl <sub>2</sub> S	$1 \times 10^{-22}$
Fe(OH) <sub>2</sub>	$4.8 \times 10^{-16}$	Zn(OH) <sub>2</sub>	$1 \times 10^{-17}$
Fe(OH) <sub>3</sub>	$3.8 \times 10^{-38}$	ZnS	$1 \times 10^{-23}$ ✓

**I, 16. Applications of the Solubility Product Relation.—**

In spite of its limitations (as outlined in the previous Section) the solubility product relation is of great value in qualitative analysis, since with its aid it is possible not only to explain but also to predict precipitation reactions. The solubility product is in reality an ultimate value which is attained by the ionic product when equilibrium has been established between the solid phase of a slightly soluble salt and the solution. If conditions are such that the ionic product is different from the solubility product, the system will seek to adjust itself in such a manner that the ionic product attains the value of the solubility product. Thus if the ionic product is arbitrarily made greater than the solubility product, for example by the addition of a small quantity of another salt with a common ion, the adjustment of the system results in the precipitation of the solid salt. Conversely, if the ionic product is made smaller than the solubility product as, for instance, by diminishing the concentration of one of the ions (see Section I, 17), equilibrium in the system is attained by some of the solid salt passing into solution.

As an example of the formation of a precipitate, let us consider the case of silver chloride. The solubility product for silver chloride is:

$$S_{\text{AgCl}}^{\text{c}} = [\text{Ag}^+] \times [\text{Cl}^-] = 1.5 \times 10^{-10}$$

Let us suppose that to a solution which is 0.1 molar in silver ions we add enough potassium chloride to produce momentarily a chloride concentration of 0.01 molar. The ionic product is then  $0.1 \times 0.01 = 1 \times 10^{-3}$ . Since  $1 \times 10^{-3} > 1.5 \times 10^{-10}$ , equilibrium will not exist and precipitation will take place ( $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}$ ) until the value of the ionic product has been reduced to that of the solubility product, *i.e.* until  $[\text{Ag}^+] \times [\text{Cl}^-] = 1.5 \times 10^{-10}$ : at this point the rate of precipitation is equal to the rate of solution of the precipitate. If now, with a saturated solution of silver chloride as the initial solution, we add either a soluble chloride or a soluble silver salt in small quantity, a slight further precipitation of silver chloride takes place: if, after equilibrium has been reached, the concentrations of the respective ions are determined, we find that, although the concentration of one ion has increased and that of the other has decreased, the ionic or solubility product is roughly constant. Some results, due to Jahn (1904), clearly illustrate this point.

TABLE I, 16, 1

EFFECT OF CHLORIDE IONS UPON THE SOLUBILITY PRODUCT OF AgCl

[KCl]	$[Cl^-] \times 10^3$	$[Ag^+] \times 10^8$	$S_{AgCl} = [Ag^+] \cdot [Cl^-] \times 10^{10}$
0.00670	6.4	1.75	1.12
0.00833	7.9	1.39	1.10
0.01114	10.5	1.07	1.12
0.01669	15.5	0.74	1.14
0.03349	30.3	0.39	1.17

A simple example is instructive.

*Example 10.* What is the concentration of silver ion in gram moles per litre remaining in solution after adding sufficient HCl to a solution of  $AgNO_3$  to make the final chloride ion concentration 0.05 molar? The solubility product of AgCl is  $1.5 \times 10^{-10}$ .

In the final solution

$$S_{AgCl} = 1.5 \times 10^{-10} = [Ag^+] \times [Cl^-] = [Ag^+] \times 0.05$$

or  $[Ag^+] = 1.5 \times 10^{-10} / 0.05 = 3.0 \times 10^{-9}$  gram mole per litre

It should be pointed out that the solubility product defines a state of equilibrium, but does not mention the rate at which equilibrium is established. Whilst the solubility product must be exceeded before precipitation can occur, this does not necessarily imply that precipitation will take place immediately. Indeed, in the formation of small amounts (say, up to 5 mg. in a volume of 10–100 ml.) of a number of insoluble salts, such as  $BaSO_4$ ,  $CuS$  and  $Mg(NH_4)PO_4$ , precipitation is not complete (and therefore equilibrium is not attained) until after 12–48 hours. Hence the statement so frequently made that precipitation occurs when the solubility product is exceeded, must have the qualification that for small amounts of precipitate some time elapses before precipitation actually begins and then a further period of variable duration must elapse before precipitation is complete.

Attention must also be drawn to the fact that *complete* precipitation of a sparingly soluble electrolyte is impossible, because no matter how much the concentration of one ion is arbitrarily increased, the concentration of the other ion cannot be decreased to zero since the S.P.\* has a constant value. The concentration of the ion can be reduced to a very small value: in *Example 10* the silver ion concentration is  $3.0 \times 10^{-9} \times 10^3$

\* The abbreviation S.P. will be employed for solubility product.

$= 3.24 \times 10^{-7}$  g. per litre, which is negligible for most practical purposes. It may be noted that in practice it is found that, after a certain point, further excess of precipitant does not materially increase the weight of the precipitate. Indeed, a large excess of precipitant may cause some of the precipitate to dissolve either as the result of increased salt effect (see Section I, 15) or as a result of complex ion formation with an ion of the precipitate (see Section I, 20). Some results of Forbes (1911), collected in the following Table, on the influence of excess of NaCl upon the solubility of AgCl illustrate this point.

TABLE I, 16, 2. EFFECT OF NaCl UPON THE SOLUBILITY OF AgCl

NaCl (moles/litre)	Ag (moles/litre) $\times 10^5$
0.933	8.6
1.433	18.4
2.272	57.0
3.000	119.4
4.170	333.5
5.039	603.9

These results show why only a *slight* excess of the reagent is added in precipitation reactions.

Having completed a limited general discussion, we are now in a position to consider some direct applications to qualitative analysis.

**Precipitation of Sulphides.** The solubility products of a number of common sulphides are: HgS  $4 \times 10^{-54}$ , PbS  $5 \times 10^{-29}$ , CuS  $1 \times 10^{-44}$ , CdS  $1.4 \times 10^{-28}$  (or  $5.5 \times 10^{-25}$ ), MnS  $1.4 \times 10^{-15}$  and ZnS  $1 \times 10^{-23}$ . When hydrogen sulphide is passed into a solution of the salts of these metals, precipitation will occur when  $[M^{++}] \times [S^{--}]$  exceeds the solubility product ( $M^{++}$  is the ion of the metal). In the usual course of qualitative analysis, the concentration of the metallic ions cannot be varied between wide limits since one is limited, on the one hand, by the solubility of the salt and, on the other hand, by the necessity of obtaining sufficient precipitate to handle and to use for qualitative tests. The concentration of the solution is of the order  $10^{-1}$  to 1 molar. The sulphide ion concentration can, however, be varied between wide limits. We have already seen that in 0.25–0.3 molar hydrochloric acid (Section I, 14,



*Example 2*), the concentration at which Group II is usually precipitated,  $[S^{--}]$  is  $1.7 \times 10^{-22}$ ; under these conditions only the solubility products of  $HgS$ ,  $PbS$ ,  $CuS$  and  $CdS$  are exceeded, and these are therefore almost completely precipitated.\* If the concentration of the acid is much higher, then  $[S^{--}]$  is reduced still further, and it is not difficult to see that  $CdS$  will be either not precipitated at all or incompletely precipitated. In a saturated aqueous solution of hydrogen sulphide,  $[S^{--}]$  is  $1 \times 10^{-14}$ , and under these conditions  $ZnS$  is partially precipitated; precipitation ceases at a certain concentration, due to the accumulation of hydrogen ions arising from the acid produced in the reaction. The increased hydrogen ion concentration decreases the dissociation of the hydrogen sulphide until  $[S^{--}]$  is such that  $[Zn^{++}] \times [S^{--}]$  is not in excess of the solubility product. For the complete precipitation of zinc sulphide, the hydrogen ions must be removed or their concentration considerably reduced; this can be achieved by the addition of sodium acetate. The latter gives rise to the feebly dissociated acetic acid ( $C_2H_3O_2^- + H^+ \rightleftharpoons H.C_2H_3O_2$ ), the  $[S^{--}]$  is maintained sufficiently high and precipitation is complete. Another method is to employ a soluble sulphide, *e.g.* ammonium or sodium sulphide, which gives a high concentration of sulphide ions in solution;  $ZnS$ ,  $MnS$  and related sulphides can then be completely precipitated.

*Example 11.* Calculate the maximum concentration of  $Cd^{++}$  ions and of  $Mn^{++}$  ions which will remain in solution after precipitation by excess of  $H_2S$  in  $0.25M$   $HCl$ . (Solubility products:  $CdS = 5.5 \times 10^{-25}$ ;  $MnS = 1.4 \times 10^{-15}$ .)

The sulphide ion concentration  $[S^{--}]$  in  $0.25M$   $HCl$  saturated with  $H_2S$  is  $1.7 \times 10^{-22}$  gram mole per litre.

Now  $[Cd^{++}] \times [S^{--}] = 5.5 \times 10^{-25}$

$[Cd^{++}] = 5.5 \times 10^{-25} / 1.7 \times 10^{-22} = 3.2 \times 10^{-3}$  gram mole  
per litre

$= 3.2 \times 10^{-3} \times 112.4 = 3.6 \times 10^{-1}$  grams per litre

Thus  $H_2S$  will precipitate about 96% of the  $Cd^{++}$  from a solution of  $0.25M$   $HCl$  containing 10 mg. of  $Cd^{++}$  per ml.

For manganese sulphide,  $[Mn^{++}] \times [S^{--}] = 1.4 \times 10^{-15}$ ;

$\therefore [Mn^{++}] = 1.4 \times 10^{-15} / 1.7 \times 10^{-22} = 8.2 \times 10^6$  gram mole  
per litre,

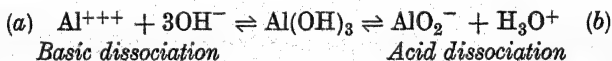
$= 8.2 \times 10^6 \times 55 = 4.5 \times 10^8$  grams per litre

This figure clearly shows that no  $MnS$  will be precipitated in  $0.25M$   $HCl$  solution.

\* A detailed calculation is given at the end of this paragraph to illustrate this point.

**Precipitation of Hydroxides.**—Here also the hydroxyl ion concentration of the precipitating agent is controlled, and the method is employed to differentiate between hydroxides of different solubility products. We have seen (Section I, 14, *Example 4*) that the addition of ammonium chloride to ammonia solution\* reduces the hydroxyl ion concentration considerably. The resultant  $[\text{OH}^-]$  is sufficient to exceed the solubility products of iron, aluminium and chromium but not of cobalt, nickel, manganese, zinc and magnesium hydroxides; the latter therefore remain in solution, whilst the former are precipitated when ammonium chloride and ammonia solution are added to a solution of their salts.

A very instructive example of the application of the solubility product principle is the **precipitation and solution of aluminium hydroxide**. The addition of hydroxyl ions in the form of sodium, potassium or ammonium hydroxides to a solution of an aluminium salt yields a white gelatinous precipitate of aluminium hydroxide, which possesses amphoteric properties. It will dissolve in solutions of caustic alkalis forming solutions of alkali aluminates, and also in solutions of acids forming the aluminium salts of the acids. The dissociation of aluminium hydroxide in aqueous solution may be expressed:



*Basic dissociation*

*Acid dissociation*

Let us now consider what will happen when excess of a strong acid, *i.e.*  $\text{H}^+$  ions, is added to a suspension of aluminium hydroxide. The acid dissociation (*b*) would be repressed on account of the common ion effect, and the basic dissociation (*a*) would be simultaneously enhanced, due to the combination of the  $\text{H}^+$  ions with the  $\text{OH}^-$  ions of the solution to form undissociated water. Initially, the ionic product of water,  $[\text{H}^+] \times [\text{OH}^-] = 1 \times 10^{-14}$ , held, but with the addition of excess of  $\text{H}^+$  ions, *i.e.* with a large increase of  $[\text{H}^+]$ , this will be momentarily exceeded. In order that the ionic product relation for water be maintained under the new experimental conditions, it will be necessary for the hydroxyl ions supplied by the aluminium hydroxide to combine with the hydrogen ions of the acid to form water. The removal of hydroxyl ions in this manner will necessitate the further dis-

\* The terms ammonia solution and ammonium hydroxide solution may be used synonymously throughout this book and refer, of course, to the aqueous solution of ammonia.

sociation of the aluminium hydroxide according to (a) since the solubility product relation

$$[\text{Al}^{+++}] \times [\text{OH}^-]^3 = S_{\text{Al(OH)}_3}$$

(the latter is very small) must hold simultaneously. Since  $[\text{H}^+]$  is very large, the further dissociation and consequent solution of the aluminium hydroxide will continue until the latter is completely dissolved.

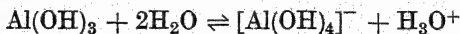
The addition of a solution of a strong base, sodium or potassium hydroxide, *i.e.* of a large hydroxyl ion concentration, will similarly repress the basic dissociation (a) and increase the acid dissociation (b), owing to combination with the hydrogen ions derived from this dissociation. It is clear that in order to maintain the ionic product of water and the solubility product of aluminium hydroxide constant under the new conditions, more  $\text{Al(OH)}_3$  must dissociate in accordance with (b); in consequence of the high hydroxyl ion concentration this process will continue until all the aluminium hydroxide has passed into solution.

The precipitation of  $\text{Al(OH)}_3$  by treating its solution in strong alkali (thus containing  $\text{AlO}_2^-$  ions) with excess of ammonium chloride solution and boiling, is readily interpreted. The effect of a large concentration of ammonium ions is to decrease the hydroxyl ion concentration owing to the formation of ammonia, a weak base; the excess of the latter is removed by boiling as ammonia gas.

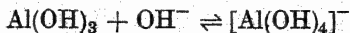


This reduction of hydroxyl ion concentration will promote the reaction (a) and bring about the combination of  $\text{H}_3\text{O}^+$  and  $\text{AlO}_2^-$  to produce a concentration of  $\text{Al(OH)}_3$  in excess of that in a saturated solution. The excess of aluminium hydroxide will then be precipitated.

The above is perhaps an over-simplified picture of the behaviour of aluminium hydroxide as an amphoteric hydroxide. The acid dissociation may also be written as:

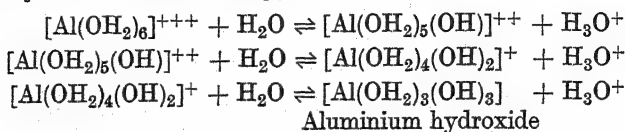


It will be noted that  $[\text{Al(OH)}_4]^-$  is a hydrated form of  $[\text{AlO}_2]^-$ , *i.e.*  $[\text{AlO}_2 \cdot \text{H}_2\text{O}]^-$ . The soluble salt  $\text{Na}[\text{AlO}_2] \cdot x\text{H}_2\text{O}$  has been isolated. The formation of an aluminate can also be represented as:



An alternative explanation of the amphoteric character of

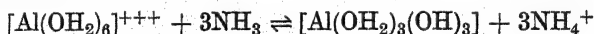
certain metallic hydroxides (see Section I, 20) has been given along the following lines. It will be illustrated by reference to aluminium hydroxide and zinc hydroxide. Some remarks concerning the hydrolysis of the aluminium ion will be given first. The aluminium ion is believed to be hydrated, *i.e.*  $[\text{Al}(\text{OH}_2)_6]^{+++}$  (compare Section I, 42) and this undergoes hydrolysis in successive stages:



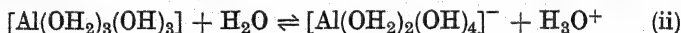
The dissolution of aluminium hydroxide in acids is merely a reversal of the hydrolysis. In basic solution, the  $\text{OH}^-$  ion withdraws a proton from the water molecules coordinated with the aluminium atom and the hydrated aluminate ion  $[\text{Al}(\text{OH})_4]^-$  is produced:



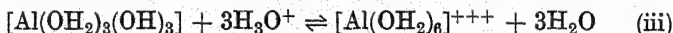
According to this scheme the precipitation of aluminium hydroxide from a solution of an aluminium salt by a base may be expressed as:



Aluminium hydroxide in water is both a proton donor (acid):

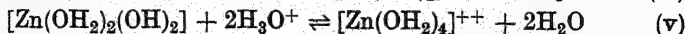
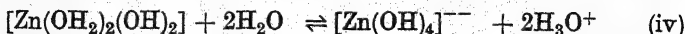


and a proton acceptor (base):

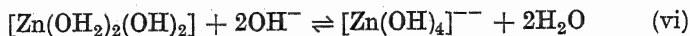


The latter process can be expressed in three stages (as above) since the aluminium hydroxide is a tri-acid base, but for simplicity the three steps have been combined into one equation. If aluminium hydroxide is treated with a strong acid, equilibrium (iii) is displaced to the left, the substance dissolves and the hydrated aluminium ion is formed. Upon adding, say, sodium hydroxide solution to a suspension of aluminium hydroxide, the  $\text{OH}^-$  ions of the solution combine with the  $\text{H}_3\text{O}^+$  ions thus displacing (ii) to the right, and the aluminate ion is produced: the ultimate reaction is expressed by (i).

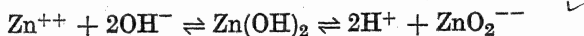
The amphoteric character of zinc hydroxide, written as  $[\text{Zn}(\text{OH}_2)_2(\text{OH})_2]$ , is explained similarly:



The over-all reaction for the dissolution of zinc hydroxide in a solution of a strong base with the formation of zincate ion is given by the following equation:



It will be noted that  $[\text{Zn}(\text{OH})_4]^{--}$  may be regarded as the hydrated zincate ion  $[\text{ZnO}_2 \cdot 2\text{H}_2\text{O}]^{--}$ . The classical representation of the amphoteric character of zinc hydroxide is:



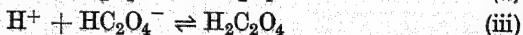
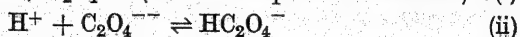
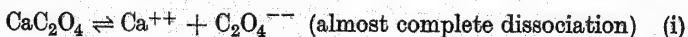
**Coprecipitation.** The discussion in the previous paragraphs gives the impression that precipitation is controlled by the solubility product principle and that the resulting precipitates are chemically pure. This, however, is not always the case. Thus, if barium sulphate is precipitated in the presence of potassium nitrate or of ferric (but not ferrous) sulphate, the precipitate is contaminated by these salts and these otherwise soluble salts cannot be removed by washing with water. The contamination of a precipitate by a substance that is normally soluble under the conditions of precipitation is termed **coprecipitation**. Other examples include the dragging down of  $\text{Ni}^{++}$  or  $[\text{Ni}(\text{NH}_3)_4]^{++}$  ions with ferric hydroxide or aluminium hydroxide, of sodium oxalate or calcium hydroxide with calcium oxalate, and of zinc hydroxide with ferric hydroxide.

If hydrogen sulphide is passed into a solution containing  $\text{Cu}^{++}$  and  $\text{Zn}^{++}$  ions which is 0.25–0.3M with respect to  $\text{H}^+$  ions, the solubility product of  $\text{CuS}$  is soon exceeded and it is therefore precipitated from solution. If the precipitate is examined immediately after precipitation, it is found to be largely pure. Upon standing, the precipitate becomes increasingly contaminated with  $\text{ZnS}$  notwithstanding the fact that the solubility product of  $\text{ZnS}$  has not been attained under the conditions of the experiment. In this case the primary precipitate separates in a more or less pure form and a second phase of foreign substance, which is slightly soluble, slowly forms subsequently. The entrainment of impurity *after* the precipitate of the desired material has been formed is termed **post precipitation**. It is usually difficult to draw a sharp line of demarcation between coprecipitation and post precipitation, but both processes are clearly responsible for the invalidation of the solubility product principle in certain cases and therefore for errors in analytical separations. Examples of post precipitation include the following: zinc sulphide and of nickel sulphide in the presence of the sulphides of mercury and of bismuth, of ferrous sulphide

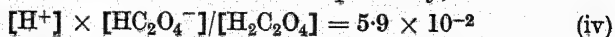
with copper sulphide, and also of magnesium oxalate in the presence of calcium oxalate.

There are many interpretations of the phenomena of coprecipitation and post precipitation, but these cannot be discussed here in detail. They may be due to adsorption on the surface of the precipitate, to mutual precipitation of colloidal particles in suspension (compare Section I, 44), to occlusion (mechanical trapping of the mother liquor containing foreign ions in the precipitate), or to substitution of one ion for another in the crystal lattice of the precipitate. The phenomena are usually specific. Coprecipitation may be diminished by making the concentration of the coprecipitated salt as small as is practicable; if the precipitant itself is dragged down, it should be diluted and added dropwise with rapid stirring. In some cases (*e.g.* calcium oxalate in the presence of magnesium ions), the contaminated precipitate is separated by filtration, partially washed, dissolved and reprecipitated. This process is termed **double precipitation**. The extent of contamination of the precipitate is a function of the concentration of the coprecipitated substance: the second precipitate is produced in a solution in which the contaminants are present in much lower concentration and thus the amount of coprecipitation is decreased considerably.

**I, 17. Solubility of Sparingly Soluble Salts of Weak Acids in Strong Mineral Acids.**—The solubility product principle enables one to give a simple explanation of this phenomenon, which is of relatively frequent occurrence in qualitative analysis. Typical examples are the solubilities of barium chromate and of calcium oxalate in dilute mineral acids, but not in acetic acid. When dilute hydrochloric acid is added in excess to a suspension of calcium oxalate in water, the following ionic equilibria will be present in solution:



The primary and secondary dissociation constants of oxalic acid are  $5.9 \times 10^{-2}$  and  $6.4 \times 10^{-5}$  respectively, *i.e.*



It is evident from equation (v) that if  $[\text{H}^+]$  is large,  $[\text{C}_2\text{O}_4^{--}]$  must be correspondingly small, and will be reduced from its

initial value in a saturated solution of calcium oxalate by combination with hydrogen ions to form first  $\text{HC}_2\text{O}_4^-$  and subsequently  $\text{H}_2\text{C}_2\text{O}_4$ . Equilibrium (i) will thus be disturbed; in order to maintain the solubility product equilibrium more calcium oxalate will pass into solution to restore that removed by reactions (ii) and (iii). If sufficient mineral acid is present, the process will continue until the whole of the calcium oxalate has dissolved.

When acetic acid is added, no reaction occurs. The ionisation constant of acetic acid,

$$[\text{H}^+] \times [\text{C}_2\text{H}_3\text{O}_2^-] / [\text{H}.\text{C}_2\text{H}_3\text{O}_2], \text{ is } 1.82 \times 10^{-5},$$

and the hydrogen ion concentration thereby introduced is not sufficiently great to influence the oxalate ion concentration in equation (v).

Similarly with barium chromate, the addition of a large excess of mineral acid reduces the chromate ion concentration by the reaction:



and consequently the substance passes into solution. (All dichromates are soluble in water.) Acetic acid, on the other hand, introduces only a very small hydrogen ion concentration and therefore has little effect. For this reason, the barium carbonate precipitate in Group IV is dissolved in dilute acetic acid, not in hydrochloric acid, before the addition of potassium chromate solution.

**I, 18. Fractional Precipitation.**—The calculation as to which of two sparingly soluble salts will be precipitated under a given set of experimental conditions may be made with the aid of the solubility product principle. An example of great practical importance is the Mohr method for the estimation of halides. In this process a solution of a chloride, *i.e.*  $\text{Cl}^-$ , is titrated with silver nitrate solution, *i.e.*  $\text{Ag}^+$ , a small quantity of potassium chromate ( $\text{CrO}_4^{--}$ ) being added to serve as an indicator. Here two sparingly soluble salts may be formed, *viz.* silver chloride and silver chromate, the solubility products of which are  $1.5 \times 10^{-10}$  and  $2.4 \times 10^{-12}$  respectively.

The following relations must be satisfied for equilibrium between the two precipitates and their solutions:

$$[\text{Ag}^+] \times [\text{Cl}^-] = 1.5 \times 10^{-10} \quad (\text{i})$$

$$[\text{Ag}^+]^2 \times [\text{CrO}_4^{--}] = 2.4 \times 10^{-12} \quad (\text{ii})$$

From (i) and (ii), one obtains:

$$\frac{[\text{Cl}^-]^2}{[\text{CrO}_4^{--}]} = \frac{(1.5 \times 10^{-10})^2}{2.4 \times 10^{-12}} = \frac{1}{1.1 \times 10^8} \quad (\text{iii})$$

Silver chromate will therefore not precipitate until its concentration, or more correctly the chromate ion concentration, is in excess of that given by this equation. It is evident that if the initial solution contains chloride and a chromate in equivalent proportions, and one adds a solution of silver nitrate dropwise, silver chloride will be precipitated until  $[\text{CrO}_4^{--}]$  is in excess of the ratio given in equation (iii); henceforth silver chromate will be precipitated with traces of silver chloride, the equilibrium ratio in (iii) being maintained in the supernatant liquid. In actual practice, the chloride ion concentration is usually approximately 0.1 molar, the silver nitrate solution about 0.1 molar and the chromate ion concentration about  $2 \times 10^{-3}$  molar (2 ml. of 0.1 molar potassium chromate solution per 100 ml. of solution). It is clear, therefore, that precipitation of silver chloride is almost complete before reaction occurs between the excess of silver ions and chromate ions to give the red silver chromate.

The following detailed calculations may prove instructive.

*Example 12.* A solution contains 0.1 gram mole  $\text{Cl}^-$  and 0.002 gram mole  $\text{CrO}_4^{--}$  per litre. Deci-molar silver nitrate solution is added gradually to this solution. Calculate: (i) whether  $\text{AgCl}$  or  $\text{Ag}_2\text{CrO}_4$  will be precipitated first, (ii) the concentration of chloride ion in solution when the  $\text{Ag}_2\text{CrO}_4$  begins to precipitate, and (iii) the fraction of the original chloride ion concentration remaining in solution when  $\text{Ag}_2\text{CrO}_4$  commences to precipitate.

$$\begin{aligned} (\text{i}) \quad S_{\text{AgCl}} &= 1.5 \times 10^{-10} = [\text{Ag}^+] \times [\text{Cl}^-] \\ &= [\text{Ag}^+] \times 0.1 \end{aligned}$$

$$\text{or } [\text{Ag}^+] = 1.5 \times 10^{-10}/0.1 = 1.5 \times 10^{-9} \text{ gram mole per litre}$$

$$S_{\text{Ag}_2\text{CrO}_4} = 2.4 \times 10^{-12} = [\text{Ag}^+]^2 \times 0.002$$

$$\text{or } [\text{Ag}^+] = \sqrt{2.4 \times 10^{-12}/0.002} = 3.5 \times 10^{-5} \text{ gram mole per litre}$$

A smaller concentration of  $\text{Ag}^+$  is required to precipitate  $\text{AgCl}$  and hence it will precipitate first.

(ii) The  $\text{Ag}^+$  concentration necessary to precipitate the  $\text{Ag}_2\text{CrO}_4$  is  $3.5 \times 10^{-5}$  gram mole per litre. The chloride ion concentration will then be:

$$\begin{aligned} [\text{Cl}^-] &= 1.5 \times 10^{-10}/[\text{Ag}^+] = 1.5 \times 10^{-10}/3.5 \times 10^{-5} \\ &= 4.3 \times 10^{-6} \text{ gram mole per litre} \end{aligned}$$



(iii) The initial  $\text{Cl}^-$  concentration is 0.1 gram mole per litre, hence  $[\text{Cl}^-]$  when  $\text{Ag}_2\text{CrO}_4$  precipitates is  $4.3 \times 10^{-6}/0.1 = 4.3 \times 10^{-5} = 0.0043$  per cent of original chloride ion concentration.

Another example of some practical interest is the precipitation of a solution containing  $\text{Sr}^{++}$  ions and  $\text{Ba}^{++}$  ions by  $\text{SO}_4^{--}$  ions. Which will be precipitated first?

● The solubility products are given by:

$$[\text{Sr}^{++}] \times [\text{SO}_4^{--}] = 2.8 \times 10^{-7} \quad (\text{iv})$$

$$[\text{Ba}^{++}] \times [\text{SO}_4^{--}] = 9.2 \times 10^{-11} \quad (\text{v})$$

These two expressions and also the relation:

$$\frac{[\text{Sr}^{++}]}{[\text{Ba}^{++}]} = \frac{2.8 \times 10^{-7}}{9.2 \times 10^{-11}} = \frac{3000}{1} \quad (\text{vi})$$

must be satisfied for equilibrium between the two precipitates. It follows therefore:

(a) if  $[\text{Sr}^{++}] > 3000 [\text{Ba}^{++}]$ , and  $\text{SO}_4^{--}$  is added,  $\text{SrSO}_4$  will be precipitated until  $[\text{Sr}^{++}] = 3000 [\text{Ba}^{++}]$ ;

(b) if  $[\text{Sr}^{++}] < 3000 [\text{Ba}^{++}]$ , and  $\text{SO}_4^{--}$  is added,  $\text{BaSO}_4$  will be precipitated until  $[\text{Sr}^{++}] = 3000 [\text{Ba}^{++}]$ .

Further addition of  $\text{SO}_4^{--}$  in either (a) or (b) will result in the precipitation of a mixture of  $\text{SrSO}_4$  and  $\text{BaSO}_4$  in the ratio of 3000 to 1, the equilibrium ratio (vi) in the supernatant liquid being maintained.

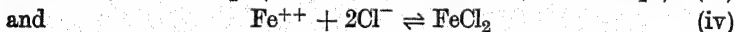
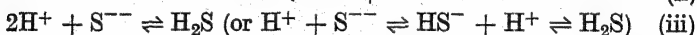
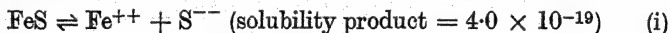
The student should carry out a similar calculation for  $\text{SrSO}_4$  and  $\text{CaSO}_4$  (solubility product  $= 2.3 \times 10^{-4}$ ): this has an important bearing upon the separation of Group IV metals (see Sections III, 32, and VII, 15).

As previously pointed out, the values of many solubility products are not known with any great accuracy: for this reason considerable caution must be exercised in predicting whether or not a given ion can be separated from one or more ions on the basis of solubility product equations, particularly when there is some doubt as to the exact magnitude of the solubility products.

**I, 19. Preparation of Solutions.**—In order to prepare a "solution" of a substance sparingly soluble in water, the process of precipitation must be reversed, *i.e.* the action of the reagent must be such as to reduce the concentration of one or both of the ions of the slightly soluble substance. The concentration of an ion can be reduced by one of the following methods: (a) the formation of a weak electrolyte or of undissociated

molecules; (b) the formation of a complex ion; (c) by double decomposition; and (d) by oxidation or reduction.

The first method is applicable to electrolytes which are derivatives of weak acids (or bases), such as barium sulphite, calcium phosphate, calcium carbonate and ferrous sulphide. If any of these substances is treated with dilute hydrochloric acid, solution occurs because of the formation of the weak acids  $\text{H}_2\text{SO}_3$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{H}_2\text{CO}_3$  and  $\text{H}_2\text{S}$ . These weak electrolytes can exist in equilibrium with only a very small concentration of their ions, and the anion concentration is diminished still further by the presence of hydrogen ions from the completely dissociated hydrochloric acid. The ionic concentration is thus reduced to so low a value that the solubility product is never exceeded, and the substance passes into solution in an attempt to restore the solubility product equilibrium. Let us consider a particular case in detail—the solution of ferrous sulphide in dilute hydrochloric acid. The ionic equilibria involved will be:



The hydrochloric acid is completely dissociated; the concentration of HCl must therefore be regarded as infinitesimally small. Combination between the  $\text{H}^+$  from the acid and the  $\text{S}^{--}$  gives the weakly ionised and slightly soluble gas  $\text{H}_2\text{S}$ ; that in excess of the solubility of the latter will be evolved as the free gas. The sulphide ion concentration is thus reduced, the equilibrium (i), controlled by

$$[\text{Fe}^{++}] \times [\text{S}^{--}] = 4.0 \times 10^{-19},$$

is disturbed. More ferrous sulphide must therefore pass into solution to restore the reduced sulphide ion concentration, but since the latter is being continually removed by the high hydrogen ion concentration, the ultimate result will be, if the acid concentration is sufficiently great, that all the ferrous sulphide will pass into solution.

The solubility of lead sulphate in saturated ammonium acetate solution is due to the formation of the feebly ionised lead acetate—a weak electrolyte (compare Section I, 17):



Furthermore, manganous, zinc and magnesium hydroxides dissolve in ammonium chloride solution owing to the formation

of the weak base, ammonia. The presence of a high concentration of ammonium ions reduces the hydroxyl ion concentration to so low a value that the solubility products of the above hydroxides cannot be attained (compare *Example 4* in Section I, 14) and they consequently pass into solution.

Numerous examples are available to illustrate method (b), but only two will be mentioned now as the subject is treated fully in Section I, 20. Silver chloride is soluble in ammonia solution, due to the formation of the complex ion  $[\text{Ag}(\text{NH}_3)_2]^+$ ; this yields so small a silver ion concentration, particularly in the presence of excess of ammonia solution, that the solubility product of silver chloride is not attained. In a similar manner silver cyanide dissolves in potassium cyanide solution, the complex ion  $[\text{Ag}(\text{CN})_2]^-$  being formed.

In method (c), the product of the reaction is either another insoluble substance or a substance which can be removed from the system by virtue of some such property as ease of decomposition or volatility. This procedure is exemplified when an insoluble salt is heated with a large excess of a saturated solution of sodium carbonate. Partial decomposition ensues with the formation of the insoluble carbonate of the cation and a solution containing the anion, together with the excess of carbonate ions. After filtration, the residue may be dissolved in dilute hydrochloric acid, and a solution, containing the cations, obtained. A specific example is the preparation of a solution of barium sulphate; the initial aqueous extract contains the sulphate ions, and the hydrochloric acid extract the barium ions.

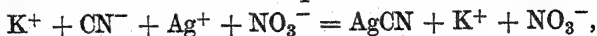
Process (d) may be illustrated by the dissolution of cupric sulphide in nitric acid. The sulphide ion  $\text{S}^{--}$  is oxidised to free sulphur  $\text{S}^0$ , the sulphide ion concentration is thereby reduced below the solubility product of  $\text{CuS}$  and hence the latter passes into solution.

**I, 20. Complex Ions.**—Reference was made in the previous section to the increase of solubility produced by the formation of complex ions. A **complex ion** is formed by the union of a simple ion with either other ions of opposite charge or with neutral molecules. Let us now examine a few examples in some detail.

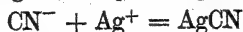
When potassium cyanide solution is added to a solution of silver nitrate, a white precipitate of silver cyanide is formed because the solubility product of silver cyanide,

$$[\text{Ag}^+] \times [\text{CN}^-] = S_{\text{AgCN}} \quad (\text{i})$$

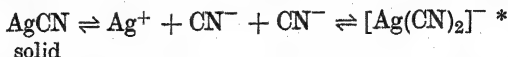
is exceeded. The reaction is expressed:



or



This precipitate dissolves upon the addition of excess of potassium cyanide, the complex ion  $[\text{Ag}(\text{CN})_2]^-$  being produced:



(or  $\text{AgCN} + \text{KCN} = \text{K}[\text{Ag}(\text{CN})_2]$ —a soluble complex salt)

This complex ion dissociates to give silver ions, since the addition of sulphide ions yields a precipitate of silver sulphide (solubility product  $1.6 \times 10^{-49}$ ), and also silver is deposited from the complex cyanide solution upon electrolysis. The complex ion thus dissociates in accordance with the equation:



By applying the law of mass action to (ii), one obtains the dissociation constant or **instability constant** of the complex ion:

$$\frac{[\text{Ag}^+] \times [\text{CN}^-]^2}{\{[\text{Ag}(\text{CN})_2]^- \}} = K \quad (\text{iii})$$

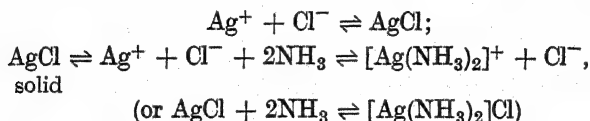
The constant has a value of  $1.0 \times 10^{-21}$  at the ordinary temperature. By inspection of this expression, and bearing in mind that an excess of cyanide ions is present, it should be evident that the silver ion concentration must be very small, so small, in fact, that the solubility product of silver cyanide is not exceeded.

The process of solution of the silver cyanide in the potassium cyanide solution may be pictured as follows. Equations (i) and (iii) control the silver ion concentrations in AgCN and the complex  $[\text{Ag}(\text{CN})_2]^-$  respectively, the former being very much greater than the latter. The concentration of silver ions derived from the saturated solution of AgCN is much greater than that permitted by equilibrium (ii); accordingly, the excess of silver ions combine with cyanide ions to form the complex  $[\text{Ag}(\text{CN})_2]^-$ . This will result in the lowering of the ionic product of AgCN, and more of the latter will pass into solution in order to supply the silver ions removed in the formation of the slightly dissociated complex ion. This process will continue either until all the AgCN has dissolved or until practically the

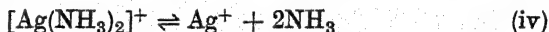
\* It is usual to employ square brackets to include the whole of a complex ion. In order to avoid confusion with concentrations for which square brackets are also widely used, concentrations will be expressed in heavy type and complex ions either in lighter type or between braces.

whole of the  $\text{CN}^-$  has reacted to form  $[\text{Ag}(\text{CN})_2]^-$ . It must be remembered that the complex salt formed,  $\text{K}[\text{Ag}(\text{CN})_2]$  is very soluble in water, and its solubility product is therefore never exceeded under the ordinary experimental conditions. This mechanism, *viz.* the formation of a feebly dissociated complex ion from one of the ions of a completely dissociated, sparingly soluble salt and another ion or neutral molecule is the basis of all the reactions of the type that are being considered.

Let us consider now the solubility of silver chloride in ammonia solution. The reactions are:



Here again, for reasons similar to those already given, silver ions are present in solution. The dissociation of the complex ion is represented by:



and the instability constant is given by:

$$\frac{[\text{Ag}^+] \times [\text{NH}_3]^2}{[\{\text{Ag}(\text{NH}_3)_2\}^+]} = K = 6.8 \times 10^{-8} \quad (\text{v})$$

The magnitude of the instability constant clearly shows that only a very small silver ion concentration is produced by the dissociation of the complex ion. It is clear from the expression for the instability constant that the concentration of  $\text{Ag}^+$  which can exist in equilibrium with  $\text{NH}_3$  is inversely proportional to the square of the concentration of ammonia. The greater the concentration of the latter, the smaller will be the concentration of silver ion. The concentration of  $\text{Ag}^+$  available from  $\text{AgCl}$  is controlled by the solubility product relation:

$$S_{\text{AgCl}} = [\text{Ag}^+] \times [\text{Cl}^-] \quad (\text{vi})$$

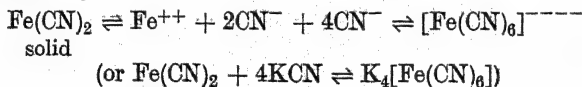
This  $[\text{Ag}^+]$  is very much greater than can exist in equilibrium with  $\text{NH}_3$ , hence the  $\text{Ag}^+$  combines with the  $\text{NH}_3$  to form some  $[\text{Ag}(\text{NH}_3)_2]^+$ . The resulting lowering of  $[\text{Ag}^+]$  will cause the ionic product  $[\text{Ag}^+] \times [\text{Cl}^-]$  to fall below the solubility product of  $\text{AgCl}$  and more  $\text{AgCl}$  must dissolve. This process will continue until all the  $\text{AgCl}$  is dissolved or until practically all the  $\text{NH}_3$  has been converted into the complex ion. Summarising, we may say that  $\text{AgCl}$  dissolves in  $\text{NH}_3$  because  $[\text{Ag}^+]$  controlled by the  $S_{\text{AgCl}}$  relationship is greater than that from the instability constant expression (v).

Silver bromide is less soluble in water than silver chloride and thus gives a smaller  $[\text{Ag}^+]$ : for this reason  $\text{AgBr}$  dissolves only slightly in dilute ammonia solution but to a larger extent in concentrated ammonia. The  $[\text{Ag}^+]$  in a saturated aqueous solution of  $\text{AgBr}$  is only slightly larger than the  $[\text{Ag}^+]$  in (iv) and consequently only a little will dissolve. With concentrated ammonia solution, the value of  $[\text{Ag}^+]$  in (iv) is so much reduced that it is considerably lower than  $[\text{Ag}^+]$  derived from  $\text{AgBr}$  hence more  $\text{AgBr}$  passes into solution. Silver iodide is much less soluble in water than silver bromide and hence it does not dissolve appreciably even in concentrated ammonia solution. The following experimental facts now have a reasonable theoretical explanation:

1. Upon adding  $\text{KBr}$  to a dilute ammoniacal solution of  $\text{AgCl}$ ,  $\text{AgBr}$  is precipitated.

2. Upon adding  $\text{KI}$  to an ammoniacal solution of  $\text{AgCl}$  or of  $\text{AgBr}$ ,  $\text{AgI}$  is precipitated.

Another familiar example is the solution of ferrous cyanide in potassium cyanide solution to yield potassium ferrocyanide or the ferrocyanide ion:



The further dissociation of the ferrocyanide ion:



is so small that no method at present known can detect either the simple ferrous ion or the cyanide ion in solution: the complex ion is an extremely stable one.

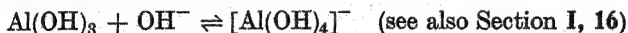
Other cyanide complex ions include the following:  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $[\text{Co}(\text{CN})_6]^{4-}$ ,  $[\text{Co}(\text{CN})_6]^{3-}$ ,  $[\text{Hg}(\text{CN})_4]^{2-}$ ,  $[\text{Cu}(\text{CN})_4]^{3-}$ ,  $[\text{Cd}(\text{CN})_4]^{2-}$ ,  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $[\text{Zn}(\text{CN})_4]^{2-}$ . The cuprous and cadmium complexes are of especial interest since they are utilised in one method for the separation of  $\text{Cu}^{++}$  and  $\text{Cd}^{++}$ . A solution containing these ions is treated with excess of ammonia solution and then with potassium cyanide solution until the blue colour of the solution is just discharged (see Section VII, 11). The resulting solution contains the completely ionised salts  $\text{K}_3[\text{Cu}(\text{CN})_4]$  (derived from cuprous copper) and  $\text{K}_2[\text{Cd}(\text{CN})_4]$ . The instability constants of  $[\text{Cu}(\text{CN})_4]^{3-}$  and  $[\text{Cd}(\text{CN})_4]^{2-}$  are  $5.0 \times 10^{-28}$  and  $1.4 \times 10^{-17}$  respectively, i.e. the former is much more stable than the latter and the  $[\text{Cu}^+]$  furnished by it is extremely small. When hydrogen sulphide

is passed into the solution CdS is precipitated (solubility product  $1.4 \times 10^{-28}$ ) but no copper sulphide (solubility products,  $\text{Cu}_2\text{S}$   $2 \times 10^{-47}$ ,  $\text{CuS}$   $1.0 \times 10^{-44}$ ) in spite of the fact that the solubility product is much smaller.

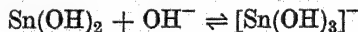
Some reference should be made to the so-called **hydroxide complex ions**. When sodium hydroxide solution is added in small quantities to a solution containing  $\text{Zn}^{++}$ , a white precipitate of zinc hydroxide is formed: this dissolves in excess of the reagent. A complex salt, sodium zincate  $\text{Na}_2[\text{ZnO}_2] \cdot 2\text{H}_2\text{O}$  or  $\text{Na}_2[\text{Zn}(\text{OH})_4]$ , is formed. The reaction is perhaps best represented as:



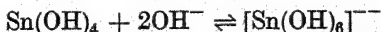
the formation of this complex ion reduces the  $\text{Zn}^{++}$  concentration with the result that the ionic product  $[\text{Zn}^{++}] \times [\text{OH}^-]^2$  is less than the solubility product and the zinc hydroxide dissolves. The complex  $\text{Na}_2[\text{Cd}(\text{OH})_4]$  is formed with difficulty and requires the use of very strong alkali. A solution containing aluminium ions behaves similarly to zinc towards sodium hydroxide solution, the initial precipitate of aluminium hydroxide dissolving in an excess of alkali to form an aluminate of the type  $\text{Na}[\text{AlO}_2] \cdot x\text{H}_2\text{O}$  or  $\text{Na}[\text{Al}(\text{OH})_4]$ :



Chromic hydroxide also behaves similarly and the complex ion may be written (by analogy) as  $[\text{Cr}(\text{OH})_4]^-$ . Stannous salts give initially a precipitate of stannous hydroxide, which dissolves in excess of alkali to form sodium stannite, variously formulated as  $\text{Na}_2[\text{SnO}_2] \cdot \text{aq.}$  or  $\text{Na}[\text{SnO} \cdot \text{OH}] \cdot \text{aq.}$  The reaction may be written:

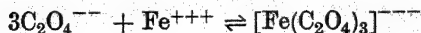


Stannic salts yield ultimately  $\text{Na}_2[\text{SnO}_3] \cdot 3\text{H}_2\text{O}$  or  $\text{Na}_2[\text{Sn}(\text{OH})_6]$ , *i.e.*



There is some evidence for the existence of the plumbite  $[\text{Pb}(\text{OH})_3]^-$  and plumbate  $[\text{Pb}(\text{OH})_6]^{--}$  ions. All the above hydroxides are amphoteric.

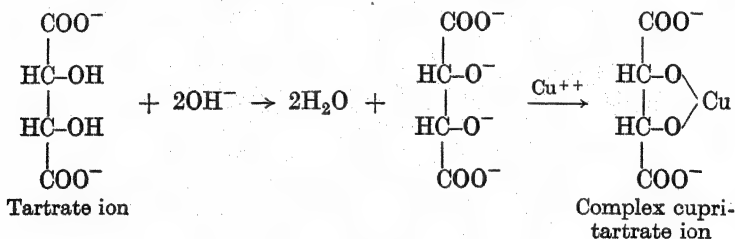
The oxalate ion forms a fairly stable complex with the ferric ion:



The  $[\text{Fe}^{+++}]$  can be reduced (by the addition of sufficient  $\text{C}_2\text{O}_4^{--}$ ) to so low a value that the solution does not give the

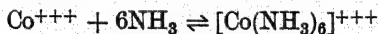
red colour of the ferri-thiocyanate ion  $[\text{Fe}(\text{SCN})]^{++}$  with a soluble thiocyanate; it does, however, yield a precipitate of ferric hydroxide when treated with sodium hydroxide solution. Upon adding a strong acid the slightly ionised  $\text{HC}_2\text{O}_4^-$  is formed, leading to the ionisation of the complex ferri-oxalate ion to such an extent that  $\text{Fe}^{+++}$  can be detected with potassium ferrocyanide or with potassium thiocyanate.

Certain non-volatile organic compounds containing hydroxyl (OH) groups, such as tartrates, citrates, sugars and glycerol, form complex ions with various metals ( $\text{Cu}^{++}$ ,  $\text{Fe}^{+++}$ ,  $\text{Al}^{+++}$ ,  $\text{Cr}^{+++}$ , etc.). In these the metal replaces the hydrogen in the hydroxyl group. Thus in an alkaline solution of a tartrate, the complex ion with  $\text{Cu}^{++}$  may be formulated thus:



These complex ions are very stable and yield such low concentrations of the simple metal ions that they often fail to respond to the simple tests of qualitative analysis. It is for this reason that involatile organic matter is destroyed before proceeding with the systematic detection of the metals.

Complex ions are formed by  $\text{Cu}^{++}$ ,  $\text{Cd}^{++}$ ,  $\text{Ni}^{++}$ ,  $\text{Co}^{+++}$  and  $\text{Zn}^{++}$  with  $\text{NH}_3$  molecules, *e.g.*



Many halide complex ions are known. These include  $[\text{HgCl}_4]^{--}$ ,  $[\text{SnCl}_6]^{--}$ ,  $[\text{SbCl}_6]^{--}$ ,  $[\text{FeF}_6]^{--}$ ,  $[\text{AlF}_6]^{--}$ ,  $[\text{AuCl}_4]^-$  and  $[\text{PtCl}_6]^{--}$ . These, and many others of different types, will be referred to in connexion with the reactions of the metallic ions.

The stability of complex ions varies within very wide limits. It is quantitatively expressed by means of the dissociation or instability constant. The more stable the complex, the smaller is the instability constant. When the complex ion is very stable, the common ionic reactions of the components are not shown. A few selected values of these constants at the ordinary temperature, determined by methods involving



potentiometric titration, are collected in Table I, 20, 1; this is instructive and also useful for reference purposes.

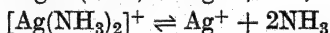
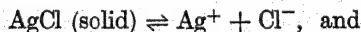
TABLE I, 20, 1. INSTABILITY CONSTANTS OF COMPLEX IONS

$[\text{Ag}(\text{NH}_3)_2]^+$	$\rightleftharpoons \text{Ag}^+ + 2\text{NH}_3$	$6.8 \times 10^{-8}$
$[\text{Ag}(\text{S}_2\text{O}_3)_2]^{--}$	$\rightleftharpoons \text{Ag}^+ + 2\text{S}_2\text{O}_3^{--}$	$1.0 \times 10^{-13}$
$[\text{Ag}(\text{CN})_2]^-$	$\rightleftharpoons \text{Ag}^+ + 2\text{CN}^-$	$1.0 \times 10^{-21}$
$[\text{Cu}(\text{CN})_4]^-$	$\rightleftharpoons \text{Cu}^+ + 4\text{CN}^-$	$5.0 \times 10^{-28}$
$[\text{Cu}(\text{NH}_3)_4]^{++}$	$\rightleftharpoons \text{Cu}^{++} + 4\text{NH}_3$	$4.6 \times 10^{-14}$
$[\text{Cd}(\text{NH}_3)_4]^{++}$	$\rightleftharpoons \text{Cd}^{++} + 4\text{NH}_3$	$2.5 \times 10^{-7}$
$[\text{Cd}(\text{CN})_4]^{--}$	$\rightleftharpoons \text{Cd}^{++} + 4\text{CN}^-$	$1.4 \times 10^{-17}$
$[\text{CdI}_4]^{--}$	$\rightleftharpoons \text{Cd}^{++} + 4\text{I}^-$	$5 \times 10^{-7}$
$[\text{HgCl}_4]^{--}$	$\rightleftharpoons \text{Hg}^{++} + 4\text{Cl}^-$	$6.0 \times 10^{-17}$
$[\text{HgI}_4]^{--}$	$\rightleftharpoons \text{Hg}^{++} + 4\text{I}^-$	$5.0 \times 10^{-31}$
$[\text{Hg}(\text{CN})_4]^{--}$	$\rightleftharpoons \text{Hg}^{++} + 4\text{CN}^-$	$4.0 \times 10^{-42}$
$[\text{Hg}(\text{SCN})_4]^{--}$	$\rightleftharpoons \text{Hg}^{++} + 4\text{SCN}^-$	$1.0 \times 10^{-22}$
$[\text{Co}(\text{NH}_3)_6]^{+++}$	$\rightleftharpoons \text{Co}^{+++} + 6\text{NH}_3$	$2.2 \times 10^{-34}$
$[\text{Co}(\text{NH}_3)_6]^{++}$	$\rightleftharpoons \text{Co}^{++} + 6\text{NH}_3$	$1.3 \times 10^{-5}$
$[\text{I}_3]$	$\rightleftharpoons \text{I}^- + \text{I}_2$	$1.4 \times 10^{-3}$
$[\text{Fe}(\text{SCN})]^{++}$	$\rightleftharpoons \text{Fe}^{+++} + \text{SCN}^-$	$3.3 \times 10^{-2}$
$[\text{Zn}(\text{NH}_3)_4]^{++}$	$\rightleftharpoons \text{Zn}^{++} + 4\text{NH}_3$	$2.6 \times 10^{-10}$
$[\text{Zn}(\text{CN})_4]^{--}$	$\rightleftharpoons \text{Zn}^{++} + 4\text{CN}^-$	$2 \times 10^{-17}$

Some examples of calculations involving complex ions should assist the student in thoroughly understanding the subject.

*Example 13.* Aqueous ammonia solution is added to a precipitate of silver chloride until its final concentration at equilibrium is 3 molar. Calculate the weight of AgCl per litre which will be dissolved. (This is equivalent to calculating the solubility of AgCl in 3M  $\text{NH}_3$ .)

The reaction is  $\text{AgCl} + 2\text{NH}_3 = [\text{Ag}(\text{NH}_3)_2]^+ + \text{Cl}^-$ ; the instability constant of the complex ion is  $6.8 \times 10^{-8}$ ;  $S_{\text{AgCl}}$  is  $1.5 \times 10^{-10}$ . Two equilibria are involved in the process of solution, viz.



At equilibrium the  $[\text{Ag}^+]$  must be the same for both provided solid AgCl and also  $[\text{Ag}(\text{NH}_3)_2]^+$  ions are present.

For each mole of AgCl dissolved, 1 mole of  $[\text{Ag}(\text{NH}_3)_2]^+$  and 1 mole of  $\text{Cl}^-$  are formed. The small value of the instability constant of the  $[\text{Ag}(\text{NH}_3)_2]^+$  ion indicates that the amount of dissociation of the complex ion is small and consequently no appreciable error will be introduced by assuming that  $[\text{Ag}(\text{NH}_3)_2]^+ = [\text{Cl}^-] = x$ , where  $x$  is expressed in mole per litre. The value of  $[\text{Ag}^+]$  at equilibrium can be obtained from:

$$S_{\text{AgCl}} = [\text{Ag}^+] \times [\text{Cl}^-] = 1.5 \times 10^{-10}$$

$$[\text{Ag}^+] = 1.5 \times 10^{-10}/x$$

Substituting the approximate values in the instability constant equation

$$\frac{[\text{Ag}^+] \times [\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2]^+} = 6.8 \times 10^{-8}$$

we have 
$$\frac{(1.5 \times 10^{-10}/x) \times 3^2}{x} = 6.8 \times 10^{-8}$$

whence 
$$x = 13.5 \times 10^{-10}/6.8 \times 10^{-8} = 0.126 \text{ mole per litre}$$
  

$$= 0.126 \times 143.3 = 18.0 \text{ gram AgCl per litre}$$

The molecular weight of AgCl is 143.3.

*Example 14.* Calculate the silver ion concentration in 0.1 molar  $[\text{Ag}(\text{NH}_3)_2]^+$  solution in which (a) excess of  $\text{NH}_3$  is absent and (b) the  $\text{NH}_3$  concentration is 3 molar.

(a) The dissociation of the complex ion is:



Let  $[\text{Ag}^+] = x$ , and hence  $[\text{NH}_3] = 2x$ . Since the dissociation of the complex ion is small, we may assume  $[\text{Ag}(\text{NH}_3)_2]^+ = 0.1$ . By substituting these values in the instability constant equation, we have:

$$x \times (2x)^2/0.1 = 6.8 \times 10^{-8}$$

or 
$$x = \sqrt[3]{6.8 \times 10^{-8}/4} = 1.9 \times 10^{-3} \text{ mole Ag}^+ \text{ per litre}$$

(b) It is evident from the instability constant equation that  $[\text{Ag}^+]$  will be inversely proportional to  $[\text{NH}_3]^2$  and therefore as  $[\text{NH}_3]$  is increased  $[\text{Ag}^+]$  will be considerably decreased. By substituting the new values for the various constants, we obtain:

$$x \times (2x + 3)^2/0.1 = x \times 3^2/0.1 = 6.8 \times 10^{-8} \text{ (since } 3 \gg x \text{)}$$

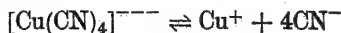
or 
$$x = 6.8 \times 10^{-8}/9 = 7.7 \times 10^{-10} \text{ mole Ag}^+ \text{ per litre}$$

*Example 15.* A 0.1 molar solution of  $[\text{Cu}(\text{NH}_3)_4]^{++}$  is stirred with an excess of potassium cyanide sufficient to convert all the ammonia complex to the corresponding cuprocyanide complex  $[\text{Cu}(\text{CN})_4]^{--}$  and in addition to provide the solution with an excess of  $\text{CN}^-$  equal to 0.2 molar. Show by calculation that when the final solution is treated with hydrogen sulphide, no precipitation of cuprous sulphide will occur.

For this calculation, let us assume that the sulphide ion concentration of the solution saturated with hydrogen sulphide is 0.001 mole per litre.\*  $S_{\text{Cu}_2\text{S}}$  is  $2.0 \times 10^{-47}$ . The instability con-

\* A saturated solution of  $\text{H}_2\text{S}$  in water is about 0.1M; this may be regarded as acting like 0.1M  $\text{K}_2\text{S}$  in the alkaline solution. The 0.1M  $\text{K}_2\text{S}$  is largely hydrolysed (see *Example 22* in Section I, 41) and gives a  $[\text{S}^{--}]$  of ca. 0.001M. The final conclusion regarding precipitation is unaffected even if the sulphide ion concentration is taken as 0.1M.

stant of the cuprocyanide ion is  $5.0 \times 10^{-28}$ . The cuprocyanide complex ion dissociates thus:



A 0.1M  $[\text{Cu}(\text{NH}_3)_4]^{++}$  solution will yield 0.1M  $[\text{Cu}(\text{CN})_4]^{---}$ . If  $x$  is the concentration of cuprous ions in moles per litre, we may substitute in the equilibrium equation with  $[\text{CN}^-] = 0.2$ :

$$\frac{[\text{Cu}^+] \times [\text{CN}^-]^4}{[\text{Cu}(\text{CN})_4]^{---}} = 5.0 \times 10^{-28} = \frac{x \times (0.2)^4}{0.1}$$

or  $x = 3.1 \times 10^{-26}$  mole per litre =  $[\text{Cu}^+]$

Now  $S_{\text{Cu}_2\text{S}} = [\text{Cu}^+]^2 \times [\text{S}^{--}] = 2.0 \times 10^{-47}$

The ionic product is  $(3.1 \times 10^{-26})^2 \times (1 \times 10^{-3}) = 9.6 \times 10^{-55}$ ; this value is less than the solubility product of  $\text{Cu}_2\text{S}$  and hence the latter is not precipitated.

## CHEMICAL EQUATIONS

The two fundamental laws of chemistry, the law of definite proportions and the law of conservation of mass, find their chief expression in practice in the form of chemical formulae and balanced equations. It is therefore of great importance that the student should be familiar with the methods of writing formulae and balancing equations. If the atomic weights are known, the percentage composition of a compound can be calculated from its chemical formula; the ratio of the weights in which substances interact and the relative weights of the products can likewise be computed from the chemical equation representing the reaction. These quantities find considerable application in the calculations of both qualitative and quantitative analysis.

**I, 21. Chemical Formulae.**—The important principle to be borne in mind when writing the more common chemical formulae is that the elements or radicals must be combined in equivalent proportions. Thus univalent elements or radicals combine (i) with other univalent elements or radicals in the ratio of 1 : 1, *e.g.*  $\text{NaCl}$ ,  $\text{NH}_4 \cdot \text{C}_2\text{H}_3\text{O}_2$ ; (ii) with bivalent atoms or radicals in the ratio of 2 : 1, *e.g.*  $\text{Na}_2\text{SO}_4$ ,  $\text{CaCl}_2$ ,  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ ; (iii) with trivalent elements or radicals in the ratio of 3 : 1, *e.g.*  $\text{FeCl}_3$ ,  $\text{H}_3\text{PO}_4$ ; and (iv) with tetravalent elements or radicals in the ratio of 4 : 1, *e.g.*  $\text{SnCl}_4$ ,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_4$ . Bivalent elements or radicals combine with other bivalent elements or radicals in the ratio of 1 : 1, *e.g.*  $\text{MgSO}_4$ ,  $\text{CaC}_2\text{O}_4$ ; with trivalent

radicals in the ratio of 3:2, *e.g.*,  $\text{Ca}_3(\text{PO}_4)_2$ ,  $\text{Al}_2(\text{SO}_4)_3$ , etc. These facts are sometimes expressed in the form of the following rule, which is applicable to normal salts: divide the least common multiple of the valencies of the two ions by the valency of each ion, and use the resulting figures as subscripts to denote the ratio in which the two ions are combined in the salt. A subscript of 1 need not be inserted. Thus in ferric sulphate, the ferric ion has a valency of 3 and the sulphate ion a valency of 2. The least common multiple is 6 and the formula is therefore  $\text{Fe}_2(\text{SO}_4)_3$ .

This rule implies a previous knowledge of the valencies of the ions or radicals, and applies only to those salts which contain one kind of positive ion in combination with one kind of negative ion. When applied to more complex compounds, such as acid salts, basic salts and double salts, the rule must be interpreted in the form that the sum of the valencies of the positive radicals (valency multiplied by the subscript for each radical) must equal the sum of the valencies of the negative radicals. Thus in basic lead acetate,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ ,  $\text{Pb}(\text{OH})_2$  or  $\text{Pb}_2(\text{C}_2\text{H}_3\text{O}_2)_2(\text{OH})_2$ , the total valency of the lead ions is 4 and the total valency of the acetate and hydroxyl radicals is also 4. In iron alum,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{Fe}_2(\text{SO}_4)_3$  or  $(\text{NH}_4)\text{Fe}(\text{SO}_4)_2$ , the positive and negative valencies are both either 8 or 4.

**I, 22, Chemical Equations.**—To construct a chemical equation one must know the formulae of the reactants and of the products of the reaction; the skeleton equation can then be written down. In order to balance the equation, the same principle as was employed in deducing the formulae of normal salts is utilised, that is, reagents interact with each other in equivalent proportions. If the latter are known, the completion of the equation is a simple matter. The difficulty, however, is in determining the number of equivalents represented by the molecular formulae of the reactants. Methods for determining these are described below.

It is convenient to divide equations into two groups (*A*) those not involving oxidation-reduction and (*B*) those that do involve oxidation-reduction (*vide infra* for definition of oxidation and reduction).

(*A*) **Equations not involving oxidation-reduction.**—The most common reaction of this class is that involving double decomposition or metathesis, *e.g.* the precipitation of barium sulphate by the action of barium chloride solution upon sulphuric acid, or the neutralisation of nitric acid with potassium hydroxide

solution. The following procedure will be found applicable to most of the examples commonly encountered:

(i) Write down the formulae of the reactants and products in the form of a skeleton equation.

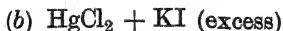
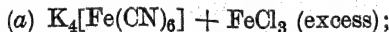
(ii) Examine the formula of the main product (or of any product more complex than the rest) to determine the reactants from which its constituents are derived.

(iii) Utilise the coefficients for the corresponding reagents that will supply these components in the correct ratio.

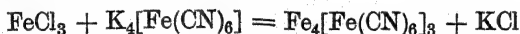
(iv) If one of the reactants supplies components for a second product, deduce the amount required for this, and add that amount to the coefficient required in (iii).

(v) Complete the equation by inspection.

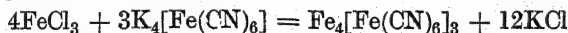
As an example we may consider the balancing of the equations:



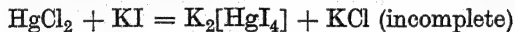
In (a) the products are ferric ferrocyanide  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  and  $\text{KCl}$ . The incomplete equation is:



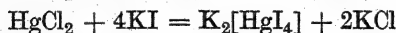
The formula  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  requires three  $[\text{Fe}(\text{CN})_6]^{---}$  and four  $\text{Fe}^{+++}$  ions, hence at least three molecules of  $\text{K}_4[\text{Fe}(\text{CN})_6]$  and four molecules of  $\text{FeCl}_3$  are required for this alone. The components of the second product  $\text{KCl}$  are supplied by the two reactants, and inspection shows that the equation is balanced by using these coefficients alone:



In (b) the products are the complex salt  $\text{K}_2[\text{HgI}_4]$  and  $\text{KCl}$ , or



The formula  $\text{K}_2[\text{HgI}_4]$  requires four atoms of iodine to one of mercury, and the formula  $\text{KCl}$  one atom of potassium to one of chlorine. The equation when written as



is balanced. If this were not the case, further adjustment of the coefficients would be necessary.

(B) **Equations involving oxidation-reduction.**—These are considered in Sections I, 24 and I, 25.

**I, 23. Discussion of Oxidation-Reduction.**—The simplest and oldest conception of oxidation involves the taking up of oxygen by an element or compound, as in the conversion of

$\text{Cu}_2\text{O}$  into  $\text{CuO}$  or of  $\text{FeO}$  into  $\text{Fe}_2\text{O}_3$ . Oxygen was the typical oxidising agent. Now  $\text{CuCl}$  and  $\text{FeCl}_2$  bear the same relation to  $\text{CuCl}_2$  and  $\text{FeCl}_3$  respectively as do the corresponding oxides to one another; it is customary, therefore, to regard the conversion of  $\text{CuCl}$  and  $\text{FeCl}_2$  into  $\text{CuCl}_2$  and  $\text{FeCl}_3$  respectively as oxidations, *i.e.* in oxidation the positive valency of an element or radical is increased.

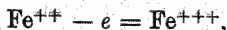
It may be noted that combination with a non-metallic element other than oxygen resembles combination with oxygen. Thus carbon burns in fluorine more vigorously than in oxygen:  $\text{C} + 2\text{F}_2 = \text{CF}_4$ . Iron burns in fluorine and, when heated, combines with chlorine and also with sulphur:  $2\text{Fe} + 3\text{F}_2 = 2\text{FeF}_3$ ;  $2\text{Fe} + 3\text{Cl}_2 = 2\text{FeCl}_3$ ;  $\text{Fe} + \text{S} = \text{FeS}$ . Owing to the similarity of these reactions to combinations with oxygen, they may clearly be regarded as a generalised sort of oxidation.

Reduction was formerly considered to be the process by which oxygen was removed from a compound. Hydrogen was regarded as the typical reducing agent. The definition can be logically extended to the process resulting in the decrease of the positive valency of an element or radical. Thus the conversion of  $\text{Fe}_2\text{O}_3$  into  $\text{FeO}$ , of  $\text{FeCl}_3$  into  $\text{FeCl}_2$ , of  $\text{CuCl}_2$  into  $\text{CuCl}$ , are examples of reduction. It is evident that the processes of oxidation and reduction are complementary; whenever one substance is oxidised, another substance must be correspondingly reduced.

Let us write the simple equation representing the oxidation of ferrous chloride by chlorine in aqueous solution:



or, expressed ionically,  $2\text{Fe}^{++} + \text{Cl}_2 = 2\text{Fe}^{+++} + 2\text{Cl}^-$ . The ferrous ion  $\text{Fe}^{++}$  is converted into the ferric ion  $\text{Fe}^{+++}$  (oxidation) and the neutral chlorine molecule into negatively charged chloride ions  $\text{Cl}^-$  (reduction). According to the electronic conception of the constitution of matter, the conversion of  $\text{Fe}^{++}$  into  $\text{Fe}^{+++}$  requires the loss of one electron, and the transformation of the neutral chlorine molecule into chloride ions necessitates the gain of two electrons. This leads to the view that, for reactions in solution, oxidation is a process involving the loss of electrons, as in



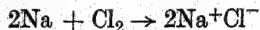
and reduction is the process resulting in the gain of electrons, as in



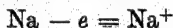
In the actual oxidation-reduction process electrons are transferred from the reducing agent to the oxidising agent.

The following are more satisfactory definitions:

**Oxidation** is the increase in the positive valency of an element or radical either by the addition of oxygen, or by the addition of chlorine or some other atom or radical which can constitute acid radicals or anions (electronegative radicals). Qualitative analysis is largely concerned with reactions in solution. The above definition may therefore be extended to ionic reactions and expressed in the form: **oxidation** is the process which results in the loss of one or more electrons by atoms or ions. An **oxidising agent** is one that gains electrons and is reduced to a lower valency condition. This electronic definition of oxidation will apply, of course, to electrovalent compounds in the solid state. Thus sodium is oxidised when it burns in chlorine to form sodium chloride:



The oxidation of the metallic sodium is the process of removing an electron from each sodium atom:



**Reduction** is the decrease in positive valency (or increase of the negative valency) either by the removal of oxygen or some electronegative atom or radical, or by the addition of an atom or radical which can constitute cations (electropositive radical). The extension of this definition to ionic reactions is: **reduction** is a process which results in the gain of one or more electrons by atoms or ions. A **reducing agent** is accordingly one that loses electrons and becomes oxidised to a higher valency condition.

Examples of oxidising agents of importance in analytical chemistry are: the halogens, potassium permanganate, potassium dichromate, nitric acid and hydrogen peroxide. Examples of reducing agents are: sulphur dioxide, hydrogen sulphide, the metals, hydrogen, stannous chloride and hydriodic acid. A detailed discussion of these is given below.

The principle referred to above, *viz.* that reagents react with one another in equivalent proportions, is employed in balancing oxidation-reduction equations. In all oxidation-reduction processes (or **redox**\* processes) there will be a reactant undergoing oxidation and one undergoing reduction, since the two reactions are complementary to one another and occur simultaneously—one cannot take place without the other. The

\* \* The simple term "redox" is an abbreviation of **reduction-oxidation**.

reagent undergoing oxidation is termed the reducing agent or **reductant**, and the reagent undergoing reduction is called the oxidising agent or **oxidant**. It is necessary to determine the number of equivalents represented by one molecule of the oxidising and reducing agent respectively, and then to assign coefficients to each such that the number of equivalents of the oxidant and of the reductant are equal. The equation can then be completed by inspection. The number of equivalents represented by one molecule of the oxidant and the reductant is determined by direct comparison. Two methods are commonly employed for this purpose; these are considered in the two sections which follow:

**I, 24. The Oxidation Number Method.**—This procedure was introduced by O. C. Johnson in 1880. It is a direct development of the view that oxidation and reduction are attended by changes of valency. The fundamental conception is the state of oxidation of the elements in particular compounds. Johnson expressed this by the term "positive or negative bond." Other authors have used "valence," "changes of valence," "valence number" and "oxidation number" to express the same quantity. The present writer prefers "oxidation number" as this term is less likely to cause confusion. The quantity is not determined by reference to any theory of atomic or molecular structure, and may be regarded as a mathematical entity deduced from an examination of the formulae of the initial and final compounds in a reaction. The **oxidation number** of an element is a number which, applied to that element in a particular compound, indicates the amount of oxidation or reduction which is required to convert one atom of the element from the *free* state into that in the compound. If oxidation is necessary to effect the change, the oxidation number is positive, and if reduction is necessary, the oxidation number is negative.

The following rules apply to the **determination of oxidation numbers**:

(1) The oxidation number of the free or uncombined element is zero. This may be written  $S^0$ ,  $Ba^0$ ,  $Cl_2^0$ , etc.

(2) The oxidation number of hydrogen in combination is, with few exceptions,  $+1$  ( $\overset{+1}{H}$ ).

\* The only exceptions are the hydrides of very electropositive metals, such as those of lithium and sodium: the oxidation number of the metal is  $+1$  and that of hydrogen is  $-1$ , e.g.  $\overset{+1}{Li} \overset{-1}{H}$ .



(3) The oxidation number of oxygen in combination is normally  $-2$  ( $\overset{-2}{\text{O}}$ ).\*

(4) The oxidation number of a metal in combination is usually positive.†

(5) The oxidation number of a radical or an ion is that of its electrovalency with the correct sign attached, *i.e.* is equal to its electrical charge.

(6) The oxidation number of a compound is always zero, and is determined by the sum of the oxidation numbers of the individual atoms each multiplied by the number of atoms of the element in one molecule.

Let us consider a few simple applications of these rules.

(i) *Oxidation number of Cu in CuO.* To convert  $\text{Cu}^0$  into  $\text{CuO}$ , the copper undergoes two units of oxidation, hence the oxidation number of the copper is  $+2$ . Alternatively, by rule 6, since oxygen is  $-2$ , copper in  $\text{CuO}$  must be  $+2$ .

(ii) *S in  $\text{H}_2\text{S}$ .* Here  $\text{H}_2 = +2$ , hence S is  $-2$ .

(iii) *N in  $\text{NH}_4\text{Cl}$ .* Consider  $\text{NH}_3$ ;  $\text{H}_3$  is  $+3$ , hence N is  $-3$ . In  $\text{HCl}$ ,  $\text{H} = +1$ , therefore Cl is  $-1$ . When  $\text{NH}_3$  and  $\text{HCl}$  combine to form  $\text{NH}_4\text{Cl}$ , the oxidation numbers of the elements in the new compound remain the same. In  $\text{NH}_4\text{Cl}$ ,  $\text{H}_4 = +4$  and  $\text{Cl} = -1$ , hence  $\text{N} = -3$ .

(iv) *N in  $\text{HNO}_3$ .* Here  $\text{O}_3 = -6$ ,  $\text{H} = +1$ , therefore  $\text{N} = +5$ .

(v) *Mn in  $\text{KMnO}_4$ .* Here  $\text{O}_4 = -8$ ,  $\text{K} = +1$ , hence  $\text{Mn} = +7$ .

(vi) *S in  $\text{SO}_4^{--}$ .* Here  $\text{O}_4 = -8$ ,  $\text{SO}_4^{--} = -2$ , hence  $-2 = -8 + \text{S}$ , or  $\text{S} = +6$ .

(vii) *C in  $\text{CO}_2$ .* Here  $\text{O}_2 = -4$ , hence  $\text{C} = +4$ .

(viii) *C in  $\text{CH}_4$ .* Here  $\text{H}_4 = +4$ , hence  $\text{C} = -4$ .

The following rules apply to the use of the oxidation number method for the balancing of equations:

(1) Determine the numerical change in oxidation number of a significant element in the oxidant.

(2) Repeat this for a corresponding significant element in the reductant.

\* The exceptions are: hydrogen peroxide and the true peroxides in which oxygen is  $-1$ , *e.g.*  $\overset{+2-2}{\text{H}_2\text{O}_2}$  and  $\overset{+2-2}{\text{Na}_2\text{O}_2}$ ; oxygen difluoride, in which the oxygen is combined with the only more electronegative element, fluorine— $\overset{+2-2}{\text{OF}_2}$ .

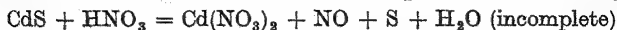
† Exceptions are to be found in the compounds with hydrogen, *e.g.*  $\overset{-4+4}{\text{GeH}_4}$ .

(3) Multiply each by coefficients which will make the total change in oxidation number equal.

(4) Inspect the skeleton equation deduced from (3), and introduce the proper coefficients for the compounds or radicals which are not oxidised or reduced.

The application to a number of examples is given below.

*Reaction I:* action of nitric acid upon cadmium sulphide.



Nitric acid:  $\text{HNO}_3$ : O.N.\* of N =  $-(-6 + 1) = +5$

Nitric oxide NO: O.N. of N =  $-(-2) = +2$ , i.e. in the reaction nitrogen changes in O.N. from  $+5$  to  $+2$ , or by 3 units of reduction.

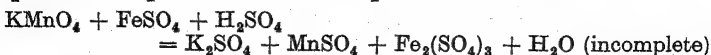
Cadmium sulphide CdS: O.N. of S =  $-(+2) = -2$ .

Free sulphur: O.N. = 0.

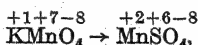
Since one molecule of  $\text{HNO}_3$  undergoes 3 units of reduction and one molecule of CdS 2 units of oxidation, the two must react in the ratio of three molecules of CdS to two molecules of  $\text{HNO}_3$ . Furthermore,  $\text{Cd}(\text{NO}_3)_2$  requires two nitrate radicals for each atom of cadmium; six more molecules of  $\text{HNO}_3$  will therefore be required to balance the equation. The latter will be:



*Reaction II:* the reduction of potassium permanganate by ferrous sulphate in the presence of dilute sulphuric acid.

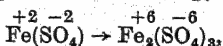


The oxidant  $\text{KMnO}_4$  is reduced to  $\text{MnSO}_4$ :



i.e. the change in O.N. of manganese is from  $+7$  to  $+2$ , or by 5 units of reduction.

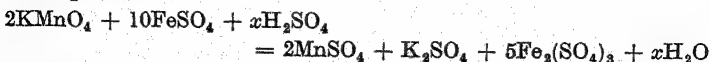
The reductant  $\text{FeSO}_4$  is oxidised to  $\text{Fe}_2(\text{SO}_4)_3$ :



i.e. the change in O.N. of one atom of iron is from  $+2$  to  $\frac{1}{2}(+6)$ , or by 1 unit of oxidation.

The  $\text{KMnO}_4$  and  $\text{FeSO}_4$  will therefore react in the ratio of 5 : 1. Now  $\text{Fe}_2(\text{SO}_4)_3$  contains two atoms of iron; the numbers of molecules in the ratio must accordingly be doubled, and are 10 : 2.

The equation becomes:

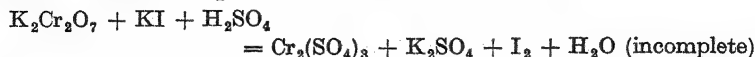


The number of sulphate radicals (after making allowance for those supplied by the  $\text{FeSO}_4$ ) required in the formation of the molecules

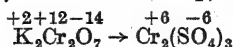
\* The term oxidation number is abbreviated to O.N.

of  $\text{MnSO}_4$ ,  $\text{K}_2\text{SO}_4$  and  $\text{Fe}_2(\text{SO}_4)_3$  is estimated by inspection, and this gives  $x = 8$ .

*Reaction III:* the interaction of potassium dichromate and potassium iodide in the presence of dilute sulphuric acid.

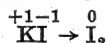


The oxidant  $\text{K}_2\text{Cr}_2\text{O}_7$  is reduced to  $\text{Cr}_2(\text{SO}_4)_3$ :



The change in O.N. of two atoms of chromium is from  $+12$  to  $+6$ , or by 6 units of reduction.

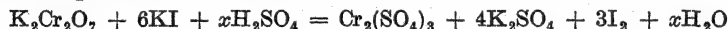
The reductant KI is oxidised to  $\text{I}_2$ :



The change in O.N. of one atom of iodine is from  $-1$  to  $0$ , or by 1 unit of oxidation.

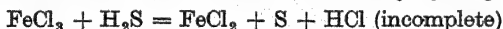
Since one molecule of  $\text{K}_2\text{Cr}_2\text{O}_7$  undergoes 6 units of reduction and one molecule of KI suffers 1 unit of oxidation, the two will react with one another in the ratio of  $\text{K}_2\text{Cr}_2\text{O}_7$ : 6KI.

The equation will therefore be:

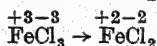


Inspection shows that  $x$  must be 7 in order to account for the number of molecules of  $\text{Cr}_2(\text{SO}_4)_3$  and  $\text{K}_2\text{SO}_4$  formed.

*Reaction IV:* the reduction of ferric chloride by hydrogen sulphide.

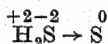


The oxidant  $\text{FeCl}_3$  is reduced to  $\text{FeCl}_2$ :



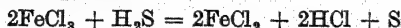
The change in O.N. of iron is from  $+3$  to  $+2$ , or by 1 unit of reduction.

The reductant  $\text{H}_2\text{S}$  is oxidised to free S:

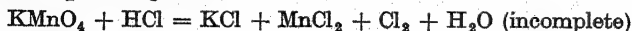


The change in O.N. of the sulphur is from  $-2$  to  $0$ , or by 2 units of oxidation.

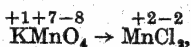
Two molecules of  $\text{FeCl}_3$  therefore react with one molecule of  $\text{H}_2\text{S}$ , and this fact, coupled with inspection of the incomplete equation, gives the balanced equation:



*Reaction V:* the action of concentrated hydrochloric acid upon potassium permanganate.

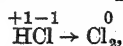


The oxidant  $\text{KMnO}_4$  is reduced to  $\text{MnCl}_2$ :



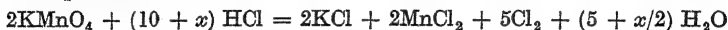
i.e. the change in O.N. of the manganese is from +7 to +2, or by 5 units of reduction.

The reductant HCl is oxidised to  $\text{Cl}_2$ :



i.e. the change in O.N. per atom of chlorine is from -1 to 0, or by 1 unit of oxidation.

The  $\text{KMnO}_4$  and HCl will therefore react in the ratio of 5 : 1. The molecule of chlorine contains two atoms; the number of molecules in the ratio must accordingly be doubled, and are 10 : 2. The equation becomes:



Inspection shows that  $x$  must be 6 in order to account for the formation of the correct number of molecules of KCl and  $\text{MnCl}_2$  derived from the  $\text{KMnO}_4$ .

**I, 25. The Ion-Electron Method.**—This method, developed in some detail by Jette and La Mer in 1927, is based upon the conception of oxidation as the loss of one or more electrons, and of reduction as the gain of one or more electrons. The method is limited to ionic reactions in aqueous solutions but, since nearly all the reactions encountered in qualitative analysis are ionic in character, the expression of chemical reactions as interaction between the ions is, for many reasons, an advantage. Furthermore, such ionic reactions can be readily converted into the molecular equations and *vice versa*.

In order to balance an ionic equation by the ion-electron method, the equation is divided into two balanced, partial equations representing the oxidation and reduction respectively. These may be regarded as corresponding to the two half cells described in Sections I, 28 and I, 33 in connexion with the theory of oxidation-reduction. It must be remembered that the reactions take place in aqueous solution so that in addition to the ions supplied by the oxidants and reductants, the molecule of  $\text{H}_2\text{O}$ ,  $\text{H}^+$  ions and  $\text{OH}^-$  ions are also present, and may be utilised in balancing the partial ionic equations. The unit change in oxidation or reduction is a change of one electron, which will be denoted by  $e$ . To appreciate the principles involved, let us study first the reaction between ferric chloride and stannous chloride in aqueous solution. The partial ionic equation for the reduction is:



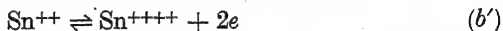
and for the oxidation is:



The equations must be balanced not only with regard to the number and kind of atoms but also electrically, that is, the net electric charge on each side must be the same. Equation (a) can be balanced by adding one electron to the left-hand side:



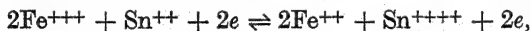
and equation (b) by adding two electrons to the right-hand side:



These partial equations must then be multiplied by coefficients which result in the number of electrons utilised in one reaction being equal to those liberated in the other. Thus equation (a') must be multiplied by two, and we have:



Adding (a'') and (b''), we obtain:



and by cancelling the electrons common to both sides, the simple ionic equation is obtained:



The following facts must be borne in mind. All strong electrolytes are completely ionised; hence only the ions actually taking part in or resulting from the reaction need appear in the equation. Substances which are only slightly ionised, such as  $\text{H}_2\text{O}$ , or which are sparingly soluble in water and thus yield only a small concentration of ions, *e.g.*  $\text{AgCl}$  and  $\text{BaSO}_4$ , are, in general, written in the molecular form because most of the substance is present in this state.

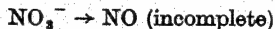
The complete rules for the application of the ion-electron method may be expressed as follows:

- (1) Ascertain the products of the reaction.
- (2) Set up a partial equation for the oxidising agent.
- (3) Set up a partial equation for the reducing agent in the same way.
- (4) Multiply each partial equation by a factor so that when the two are added the electrons just compensate each other.
- (5) Add the partial equations and cancel out substances which appear on both sides of the equation.

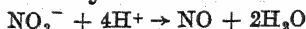
A few detailed examples follow.

*Reaction I:* action of nitric acid upon cadmium sulphide.

One partial equation (reduction) is:



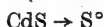
To balance this atomically one must write:



To balance the latter equation electrically,  $3e$  must be added to the left-hand side:



The second partial equation (oxidation) is:



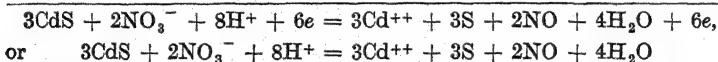
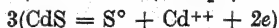
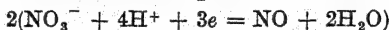
This must be written as:



to balance atomically, and as:

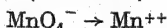


to balance electrically. Thus one nitrate ion requires 3 electrons, and one molecule of cadmium sulphide liberates 2 electrons; the two partial reactions will take place in the ratio of 2 : 3.

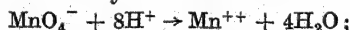


*Reaction II:* the reduction of potassium permanganate by ferrous sulphate in the presence of dilute sulphuric acid.

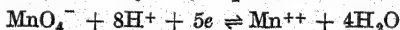
The first partial equation (reduction) is:



To balance this atomically one needs  $8\text{H}^+$ :



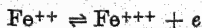
and to balance it electrically one requires  $5e$  on the left-hand side:



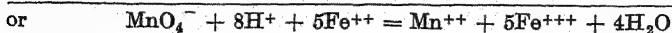
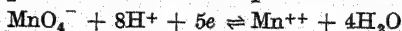
The second partial equation (oxidation) is:



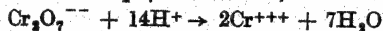
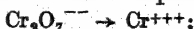
To balance this electrically one must add one electron to the right-hand side (or subtract one electron from the left-hand side):



Now the gain and loss of electrons must be equal. One permanganate ion uses 5 electrons, and one ferrous ion liberates 1 electron; hence the two partial reactions take place in the ratio of 1 : 5.



*Reaction III:* the interaction of potassium dichromate and potassium iodide in the presence of dilute sulphuric acid.



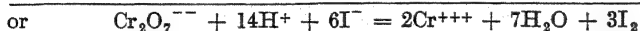
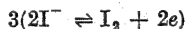
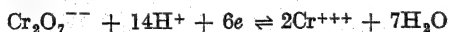
To balance electrically, add  $6e$  to the left-hand side:



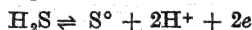
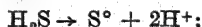
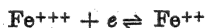
The various stages in the deduction of the second partial equation are:



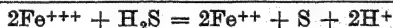
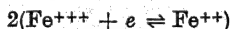
One dichromate ion uses  $6e$ , and two iodide ions liberate  $2e$ ; hence the two partial reactions take place in the ratio of 1 : 3.



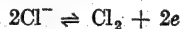
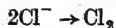
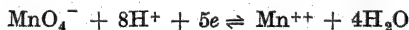
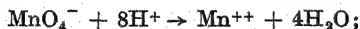
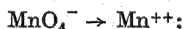
*Reaction IV:* the reduction of ferric chloride by hydrogen sulphide.



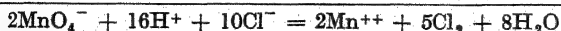
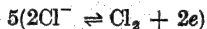
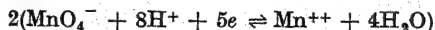
Thus one ferric ion liberates 1 electron, and one molecule of hydrogen sulphide uses 2 electrons. The partial reactions will therefore take place in the ratio of 2 : 1.



*Reaction V:* the action of concentrated hydrochloric acid upon potassium permanganate.



One permanganate ion utilises  $5e$ , and two chloride ions liberate  $2e$ , hence the two partial reactions take place in the ratio of 2 : 5.



The advantages of the ion-electron method are:

(i) The final equation gives only the substances which react and are produced in the redox reaction.

(ii) The method is free from hypothesis regarding the distribution of the valency bonds among the individual atoms constituting the oxidant and reductant. Thus with permanganates, it is not heptavalent manganese  $\text{Mn}^{\text{VII}}$  which is the oxidant but the  $\text{MnO}_4^-$  ion, the concentration of which may be experimentally determined and controlled.

(iii) The influence of the hydrogen ion (or hydroxonium ion) concentration, while not apparent in the oxidation number procedure, is clearly emphasised.

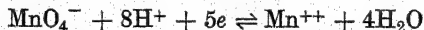
(iv) The equations are not hypothetical: indeed, they have an experimental basis.

The student should experience little difficulty in balancing the common equations by the ion-electron method and converting them into molecular equations. A brief résumé will now be given of a few typical oxidising and reducing agents and the reactions which they undergo. This will be useful for reference purposes. The reader should attempt to deduce the ionic equations independently, and also to formulate the corresponding molecular equations.

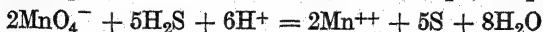
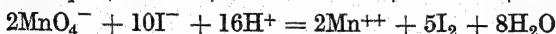
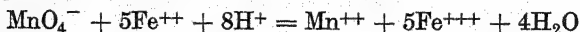
## I, 26. TYPICAL OXIDISING AND REDUCING AGENTS: SUMMARY

### OXIDISING AGENTS

**Potassium permanganate.** Its action depends upon the conversion of the manganese into a manganese compound with a lower valency or with a lower oxidation number. In acid solution, the oxidation number of manganese changes from +7 to +2, or by 5 units of reduction. Expressed ionically,  $\text{MnO}_4^-$  is converted into  $\text{Mn}^{++}$ ; this involves a gain of 5 electrons.



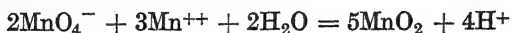
Some of the ionic reactions which potassium permanganate undergoes, are:



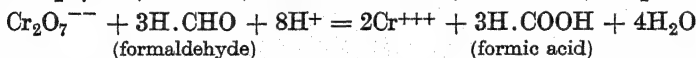
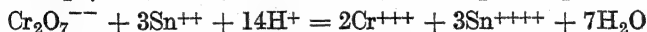
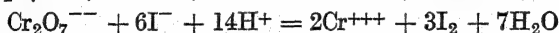
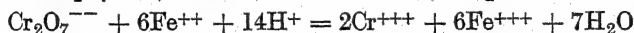
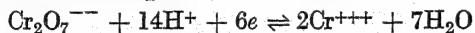
In neutral or alkaline solution, the manganese in the permanganate is generally reduced to  $\text{MnO}_2$ , i.e. by 3 units of



reduction. Ionically expressed, the change of  $\text{MnO}_4^-$  into  $\text{MnO}_2$  corresponds to a gain of 3 electrons. An example of this is the oxidation of manganese salts to  $\text{MnO}_2$ , to which the permanganate ion is itself reduced.

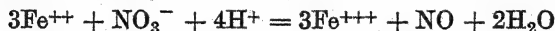
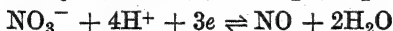
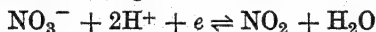


**Potassium dichromate.** Its action depends upon the conversion of the chromium into a chromic compound. In acid solution, the O.N. of two atoms of chromium changes from +12 to +6, or by 6 units of reduction. Ionically expressed,  $\text{Cr}_2\text{O}_7^{--}$  is converted into  $2\text{Cr}^{+++}$ , and this corresponds to a gain of 3 electrons per atom of chromium.

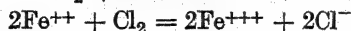


**Nitric Acid.** The oxidising action is dependent upon the reduction of the nitrogen. The nature of the reduction varies with the concentration of the acid and with the compound to be oxidised. The most common product is nitric oxide, but nitrogen dioxide, nitrous oxide, nitrogen and ammonia are also formed under different experimental conditions.

In the conversion of the nitrogen in nitric acid into nitric oxide, the O.N. changes from +5 to +2, or by 3 units of reduction. Expressed ionically, the transformation of  $\text{NO}_3^-$  into NO results in a gain of 3 electrons.



**The halogens.** Here the action is dependent upon the conversion of the neutral and free halogen into halogen ions by accepting electrons.



The oxidising action of *aqua regia* may be ascribed to the free chlorine which is liberated in the reaction:

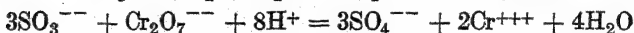
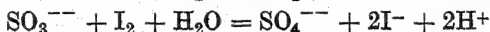
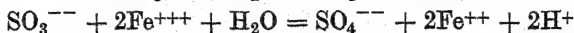
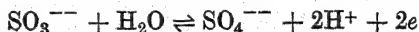


**Hydrogen peroxide.** This substance acts as both an oxidising and reducing agent. The former action, particularly in acid solution, is usually attributed to the presence of one atom of oxygen differing in its mode of attachment from the other oxygen atom.

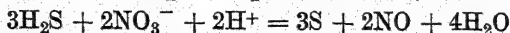
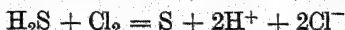
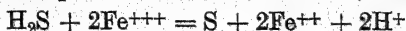
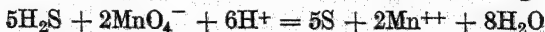
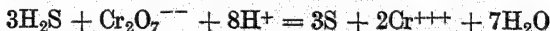


#### REDUCING AGENTS

**Sulphur dioxide or sulphurous acid.** The reducing action is dependent upon the conversion of the sulphite ion into the sulphate ion. Often the reagent is employed by adding sodium sulphite to the slightly acidified solution to be reduced. The O.N. of the sulphur changes from +4 to +6, or by two units of oxidation. Expressed ionically, the  $\text{SO}_3^{--}$  ion passes into the  $\text{SO}_4^{--}$  ion, and this corresponds to a loss of 2 electrons per atom of sulphur.



**Hydrogen sulphide.** The action depends upon the conversion of the sulphur with an O.N. of -2 into free sulphur with an O.N. of zero, i.e. by 2 units of oxidation. Expressed ionically, the change involves the loss of 2 electrons per molecule of hydrogen sulphide.



**Hydriodic acid.** Here the iodine ion passes into free iodine; the O.N. changes from -1 to 0, or by 1 unit of oxidation. This is equivalent to the loss of 1 electron.

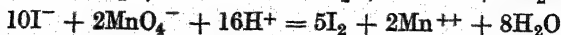
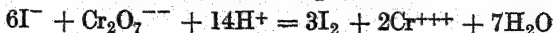
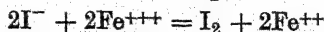
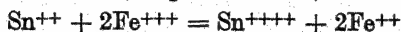
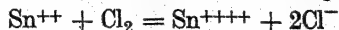
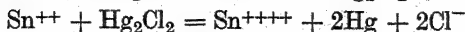
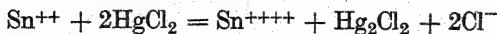


TABLE I, 26, 1

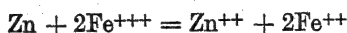
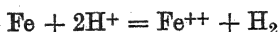
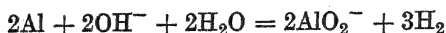
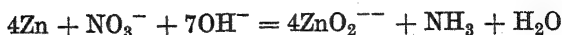
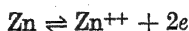
COMMON OXIDISING AGENTS						
Substance	Radical or element involved	O.N. of "effective" element	Reduction product	New O.N.	Decrease in O.N.	Gain in electrons
KMnO <sub>4</sub> (acid)	MnO <sub>4</sub> <sup>-</sup>	+7	Mn <sup>++</sup>	+2	5	5
KMnO <sub>4</sub> (alkaline)	MnO <sub>4</sub> <sup>-</sup>	+7	MnO <sub>2</sub> (or Mn <sup>++++</sup> )	+4	3	3
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	Cr <sub>2</sub> O <sub>7</sub> <sup>-</sup>	+6	Cr <sup>+++</sup>	+3	3	3
HNO <sub>3</sub> (dil.)	NO <sub>3</sub> <sup>-</sup>	+5	NO	+2	3	3
HNO <sub>3</sub> (conc.)	NO <sub>3</sub> <sup>-</sup>	+5	NO <sub>2</sub>	+4	1	1
Cl <sub>2</sub>	Cl	0	Cl <sup>-</sup>	-1	1	1
Br <sub>2</sub>	Br	0	Br <sup>-</sup>	-1	1	1
I <sub>2</sub>	I	0	I <sup>-</sup>	-1	1	1
3HCl: 1HNO <sub>3</sub>	Cl	0	Cl <sup>-</sup>	-1	1	1
H <sub>2</sub> O <sub>2</sub>	O	0	O <sup>-</sup>	-2	2	2
Na <sub>2</sub> O <sub>2</sub>	O	0	O <sup>-</sup>	-2	2	2
KClO <sub>3</sub>	ClO <sub>3</sub> <sup>-</sup>	+5	Cl <sup>-</sup>	-1	6	6
KBrO <sub>3</sub>	BrO <sub>3</sub> <sup>-</sup>	+5	Br <sup>-</sup>	-1	6	6
KIO <sub>3</sub>	IO <sub>3</sub> <sup>-</sup>	+5	I <sup>-</sup>	-1	6	6
NaOCl	OCl <sup>-</sup>	+1	Cl <sup>-</sup>	-1	2	2

COMMON REDUCING AGENTS						
Substance	Radical or element involved	O.N. of "effective" element	Oxidation product	New O.N.	Increase in O.N.	Loss in electrons
H <sub>2</sub> SO <sub>3</sub> or Na <sub>2</sub> SO <sub>3</sub>	SO <sub>3</sub> <sup>-</sup>	+4	SO <sub>4</sub> <sup>-</sup>	+6	2	2
H <sub>2</sub> S	S <sup>-</sup>	-2	S <sup>0</sup>	0	2	2
HI	I <sup>-</sup>	-1	I <sup>0</sup>	0	1	1
SnCl <sub>2</sub>	Sn <sup>++</sup>	+2	Sn <sup>++++</sup>	+4	2	2
Metals, e.g. Zn	Zn	0	Zn <sup>++</sup>	+2	2	2
Hydrogen	H	0	H <sup>+</sup>	+1	1	1
FeSO <sub>4</sub> (or any ferrous salt)	Fe <sup>++</sup>	+2	Fe <sup>+++</sup>	+3	1	1
Na <sub>2</sub> AsO <sub>3</sub>	AsO <sub>3</sub> <sup>-</sup>	+3	AsO <sub>4</sub> <sup>-</sup>	+5	2	2
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	C <sub>2</sub> O <sub>4</sub> <sup>-</sup>	+3	CO <sub>2</sub>	+4	1	1

**Stannous chloride.** The reducing action, which usually occurs in acid solution, is dependent upon the facile conversion of stannous ions into stannic ions; the change in O.N. is from +2 to +4, or by 2 units of oxidation. This is equivalent to the loss of 2 electrons.



**Metals and hydrogen.** The use of metals and of hydrogen as reductants is based upon the conversion of the metal and of neutral hydrogen into cations. The change requires an increase in O.N., or a loss of electrons, dependent upon the valency of the metal. With hydrogen, the increase in O.N. is 1 for each atom, and this corresponds to a loss of 1 electron. The reduction may take place in neutral, acid or alkaline solution.



A useful summary of the common oxidising and reducing agents, together with the various transformations which they undergo, is given in Table I, 26, 1.

**I, 27. Concentration of Reagents. Molar and Normal Solutions.**—In order to carry out an analysis in a truly scientific manner, it is necessary to know not only the reactions of the different anions and cations, but also the sensitiveness of each reaction, that is, the smallest amount of substance which can be detected under a standard set of experimental conditions. One should be able to estimate from the size of a precipitate the approximate amount of reacting ion which is present in the original substance. This, of course, will only be possible when the tests are carried out with known quantities of the reagent. For this reason, experiments are made with reagents of known strength. It is the purpose of this section to discuss the two important methods of expressing the concentration of solutions.

**Molar Solutions.** A molar solution is one which contains one gram molecular weight (or one mole) of solute per litre of solution. Thus a molar solution of potassium chloride contains  $39 + 35.5 = 74.5$  grams of KCl per litre; a molar solution of sodium sulphate decahydrate contains  $46 + 32 + 64 + 180 = 322$  grams of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  per litre.

This term is also applied to *ions* in solution, since, as their osmotic and other properties indicate, they possess some of the properties of molecules. The gram molecular weights of  $\text{H}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{--}$  and  $\text{PO}_4^{---}$  ions are 1, 35.5, 96 and 95 grams respectively. A molar solution of hydrogen ions, chloride ions,

sulphate ions or phosphate ions contains respectively 1, 35.5, 96 and 95 grams per litre of solution.

**Normal Solutions.** A normal solution contains one gram-equivalent weight of the solute per litre of solution. For convenience of manipulation, the concentration of solutions employed in qualitative analysis often contain multiples or fractions of the equivalent weight per litre, *e.g.* five times normal which is represented as  $5N$ , or one-tenth normal,  $0.1N$ . The **gram equivalent weight** is most simply defined as that weight of substance which will react with or displace 1.008 grams of hydrogen, 8 grams of oxygen, 35.5 grams of chlorine or that quantity of any element which reacts with these weights of hydrogen, oxygen and chlorine respectively. Usually the equivalent of an element is equal to its atomic weight divided by its valency. The **equivalent weight of a compound** is that weight which contains one gram equivalent weight of the component taking part in the reaction under consideration. This is generally the chief component. With acids, it is the ionisable and replaceable hydrogen; with bases, it is the ionisable hydroxyl group, and with salts, it is generally the cation or anion. The above statements apply to the simplest cases, that is, those in which no oxidation or reduction occurs. In general, the gram equivalent weight will depend upon the particular reaction in which the substance takes part. It often happens that the same compound will possess different equivalent weights in different chemical reactions. The situation may therefore arise in which a solution may have normal concentration when employed for one purpose, and a different normal concentration when used in another chemical reaction.

The **equivalent weight\*** of an acid is that weight of it which contains one replaceable hydrogen atom, *i.e.* 1.008 grams of hydrogen. The equivalent weight of a monobasic acid, such as hydrochloric, hydrobromic, hydriodic, nitric or acetic acid, is identical with the molecular weight. A normal solution of a monobasic acid will therefore contain one gram molecular weight (or 1 mole) in a litre of solution. The equivalent weight of a dibasic acid (*e.g.*  $H_2SO_4$ ) or of a tribasic acid (*e.g.*  $H_3PO_4$ ) is likewise  $1/2$  and  $1/3$  respectively of the molecular weight.

The **equivalent weight of a base** is that weight of it which contains one replaceable hydroxyl group, *i.e.* 17.008 grams of ionisable hydroxyl. 17.008 grams of hydroxyl are equivalent

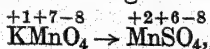
\* Throughout this volume the terms *equivalent weight* and *molecular weight* will be used synonymously with *gram equivalent weight* and *gram molecular weight* respectively.

to 1.008 grams of hydrogen. The equivalent weights of NaOH, KOH and  $\text{NH}_4\text{OH}$  (or  $\text{NH}_3$ —the Arrhenius definitions suffice for most purposes) are 1 mole, and of  $\text{Ca}(\text{OH})_2$ ,  $\text{Sr}(\text{OH})_2$  and  $\text{Ba}(\text{OH})_2$  1/2 mole.

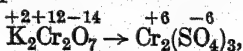
The equivalent weight of a normal salt is that weight of it which contains one gram equivalent weight of the cation or anion. This quantity will be the molecular weight of the salt divided by the total valency of the cation or anion. Thus the equivalent weight of KCl is 1 mole, of  $\text{Na}_2\text{SO}_4$  1/2 mole, of  $\text{AlCl}_3$  1/3 mole, of  $\text{SnCl}_4$  1/4 mole and of  $\text{Ca}_3(\text{PO}_4)_2$  1/6 mole.

For acid and double salts, the equivalent weight may vary with the component to which the equivalent is referred. Thus for the salt  $\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O}$ , which yields the ions  $2\text{Na}^+$ ,  $\text{HAsO}_4^{--}$ ,  $\text{H}^+$  and  $\text{AsO}_4^{---}$  upon progressive ionisation the equivalent will be 1/2 mole when referred to  $\text{Na}^+$  or  $\text{HAsO}_4^{--}$ , 1 mole when referred to  $\text{H}^+$ , and 1/3 mole when referred to  $\text{AsO}_4^{---}$ . With a double salt, like chrome alum  $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  the equivalent weight will be 1/2, 1/6 and 1/8 mole respectively according as to whether the reacting component is  $\text{K}^+$ ,  $\text{Cr}^{+++}$  or  $\text{SO}_4^{--}$ . It must clearly be pointed out that the above remarks apply only to the calculation of the equivalents of salts which do not function as oxidising or reducing agents. The equivalent weight of an acid or double salt, which does not act as an oxidant or reductant, is the gram molecular weight divided by the total valency of the reacting constituent.

✓ The equivalent weight of an oxidising agent is determined by the change in oxidation number which the reduced element experiences. It is that quantity of oxidant which involves a change of one unit in the oxidation number.\* Thus in the normal reduction of potassium permanganate in the presence of dilute sulphuric acid to a manganous salt,



the change in oxidation numbers of the manganese is from +7 to +2, or by 5 units of reduction. The equivalent weight is therefore 1/5 mole (compare Sections I, 24 and I, 26). Similarly for the reduction of potassium dichromate in acid solution,



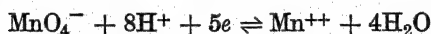
\* The standard of reference may be taken as the reaction:



This involves unit change in oxidation number. Incidentally this equation clearly shows the relation between the oxidation number method and the ion-electron method for deducing equivalent weights.

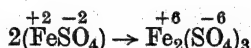
the change in O.N. of two atoms of chromium is from +12 to +6, or by 6 units of reduction. The equivalent weight of  $K_2Cr_2O_7$  is accordingly  $1/6$  mole. In order to find the equivalent weight of an oxidising agent, one divides the molecular weight by the total change in O.N. *per molecule* which some element in the substance undergoes.

We may also employ the ion-electron method (Section I, 25). The partial ionic equation in which the oxidising agent takes part is first written down. For potassium permanganate in acid solution, this is:

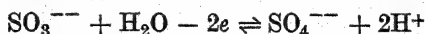


The equivalent weight of an oxidising agent in a particular reaction is then that weight of the oxidant which is associated with a gain of one electron in that reaction. In the example under consideration 5 electrons are gained, hence the equivalent weight is  $1/5$  mole. In general, to calculate the equivalent weight of an oxidising agent for a particular reaction, one divides the gram molecular weight by the number of electrons per molecule indicated in the partial ionic equation as taking part in the reaction.

The equivalent weight of a reducing agent is similarly determined by the change in oxidation number which the oxidised element suffers. Consider the conversion of ferrous into ferric sulphate:



Here the change in O.N. *per atom* of iron is from +2 to +3, or by 1 unit of oxidation, hence the equivalent weight of ferrous sulphate is 1 mole. The ion-electron method may also be employed; the procedure is exactly analogous to that described under oxidising agents. One example will be studied, *viz.* the conversion of sodium sulphite into sodium sulphate. The partial ionic equation is:



Two electrons are lost per gram molecular weight of sodium sulphite; the equivalent weight is accordingly  $1/2$  mole.

In general, it may be stated: (i) The equivalent weight of an element taking part in an oxidation-reduction (redox) reaction is the atomic weight divided by the change in oxidation number. (ii) When an atom in any complex molecule suffers a change in oxidation number (oxidation or reduction), the equivalent weight of the molecule is the molecular weight

divided by the change in oxidation number of the oxidised or reduced element. If more than one atom of the reactive element is present, the molecular weight is divided by the total change in O.N.

For convenience of reference the partial ionic equations for a number of oxidising and reducing agents are collected in Table I, 27, 1 (compare Table I, 26, 1).

TABLE I, 27, 1. IONIC EQUATIONS FOR USE IN THE CALCULATION OF THE EQUIVALENT WEIGHTS OF OXIDISING AND REDUCING AGENTS

Substance	Partial Ionic Equation
OXIDANTS	
Potassium permanganate (acid)	$\text{MnO}_4^- + 8\text{H}^+ + 5e \rightleftharpoons \text{Mn}^{++} + 4\text{H}_2\text{O}$
Potassium permanganate (neutral)	$\text{MnO}_4^- + 2\text{H}_2\text{O} + 3e \rightleftharpoons \text{MnO}_2 + 4\text{OH}^-$
Potassium dichromate	$\text{Cr}_2\text{O}_7^{--} + 14\text{H}^+ + 6e \rightleftharpoons 2\text{Cr}^{+++} + 7\text{H}_2\text{O}$
Ceric sulphate	$\text{Ce}^{++++} + e \rightleftharpoons \text{Ce}^{+++}$
Chlorine	$\text{Cl}_2 + 2e \rightleftharpoons 2\text{Cl}^-$
Ferric chloride	$\text{Fe}^{+++} + e \rightleftharpoons \text{Fe}^{++}$
Potassium iodate	$\text{IO}_3^- + 6\text{H}^+ + 6e \rightleftharpoons \text{I}^- + 3\text{H}_2\text{O}$
Sodium hypochlorite	$\text{ClO}^- + \text{H}_2\text{O} + 2e \rightleftharpoons \text{Cl}^- + 2\text{OH}^-$
Hydrogen peroxide	$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e \rightleftharpoons 2\text{H}_2\text{O}$
Manganese dioxide	$\text{MnO}_2 + 4\text{H}^+ + 2e \rightleftharpoons \text{Mn}^{++} + 2\text{H}_2\text{O}$
Sodium bismuthate	$\text{BiO}_3 + 6\text{H}^+ + 2e \rightleftharpoons \text{Bi}^{+++} + 3\text{H}_2\text{O}$
Nitric acid (conc.)	$\text{NO}_3 + 2\text{H}^+ + e \rightleftharpoons \text{NO}_2 + \text{H}_2\text{O}$
Nitric acid (dil.)	$\text{NO}_3 + 4\text{H}^+ + 3e \rightleftharpoons \text{NO} + 2\text{H}_2\text{O}$

REDUCTANTS	
Hydrogen	$\text{H}_2 - 2e \rightleftharpoons 2\text{H}^+$
Zinc	$\text{Zn} - 2e \rightleftharpoons \text{Zn}^{++}$
Hydrogen sulphide	$\text{H}_2\text{S} - 2e \rightleftharpoons 2\text{H}^+ + \text{S}$
Hydrogen iodide	$2\text{HI} - 2e \rightleftharpoons \text{I}_2 + 2\text{H}^+$
Oxalic acid	$\text{C}_2\text{O}_4^{--} - 2e \rightleftharpoons 2\text{CO}_2$
Ferrous sulphate	$\text{Fe}^{++} - e \rightleftharpoons \text{Fe}^{+++}$
Sulphurous acid	$\text{H}_2\text{SO}_3 + \text{H}_2\text{O} - 2e \rightleftharpoons \text{SO}_4^{--} + 4\text{H}^+$
Stannous chloride	$\text{Sn}^{++} - 2e \rightleftharpoons \text{Sn}^{++++}$
Stannous chloride (in presence of hydrochloric acid)	$\text{Sn}^{++} + 6\text{Cl}^- - 2e \rightleftharpoons \text{SnCl}_6^{--}$
Hydrogen peroxide	$\text{H}_2\text{O}_2 - 2e \rightleftharpoons 2\text{H}^+ + \text{O}_2$
Sodium thiosulphate	$2\text{S}_2\text{O}_3^{--} - 2e \rightleftharpoons \text{S}_4\text{O}_6^{--}$

We are now in a position to understand more clearly why the equivalent weights of substances vary with the reaction. A normal solution of ferrous sulphate  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  will have

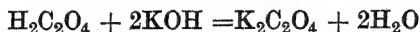


an equivalent weight of 1 mole when employed as a reducing agent and 1/2 mole when employed as a normal salt or precipitant. A solution of ferrous sulphate which is normal as a salt will be  $N/2$  as a reducing agent. A few other examples are collected below.

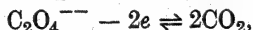
**Oxalic Acid.**  $\text{H}_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O}$ . This compound contains two replaceable hydrogen atoms, hence a normal solution contains 1/2 mole per litre.



or

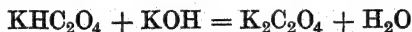


As a reducing agent, the partial ionic equation is:



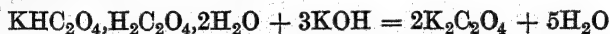
so that the equivalent weight is 1/2 mole.

**Potassium hydrogen oxalate.**  $\text{KHC}_2\text{O}_4$ . This substance has one replaceable hydrogen atom, hence, as an acid, the equivalent is 1 mole:



When functioning as a reducing agent, the reducing power is due to the  $\text{C}_2\text{O}_4^{--}$ , and the equivalent is 1/2 mole.

**Potassium tetroxalate.**  $\text{KHC}_2\text{O}_4, \text{H}_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O}$ . This salt contains three replaceable hydrogen atoms, and its equivalent weight is therefore 1/3 mole.



As a reducing agent, a gram molecular weight contains  $2\text{C}_2\text{O}_4^{--}$  and the equivalent weight is therefore 1/4 mole. A solution of this salt which is  $3N$  as an acid is  $4N$  as a reducing agent.

**Potassium permanganate.**  $\text{KMnO}_4$ . As a salt, that is, as a precipitant, the equivalent weight is 1 mole. We have already seen (Section I, 26; Tables I, 26, 1 and I, 27, 1) that the equivalent weight in acid solution is 1/5 mole, and in neutral or alkaline solution 1/3 mole. A solution of  $\text{KMnO}_4$  which is  $0.1N$  as a precipitant, is  $0.5N$  as an oxidising agent in acid solution, and  $0.3N$  as an oxidising agent in neutral or alkaline solution.

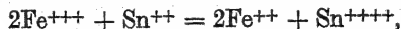
Once the reader has grasped the above concepts as to the calculation of equivalent weights he should experience no difficulty in computing the exact amount of substance required in the preparation of any solution required in qualitative analysis. The strengths of the reagents employed, together with details for their preparation, are collected in the Appendix (Section A, 2).

## I, 28. THEORY OF OXIDATION AND REDUCTION

Reference has already been made in Section I, 23 to the fact that oxidation consists of the loss of electrons and reduction of the gain of electrons. Thus in the reduction of ferric chloride by stannous chloride:



or



for every atomic weight (56 grams) of iron reduced 96,500 coulombs or 1 Faraday of electricity is lost by the iron, and for every atomic weight (119 grams) of tin oxidised, the latter has gained  $2 \times 96,500$  coulombs or 2 Faradays.\*

According to modern theory, an electric current is essentially a flow of negative electrons. It should therefore be possible to

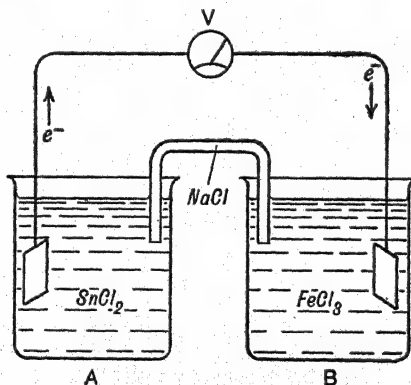


Fig. I, 28, 1

obtain direct proof of the transfer of electrons in the oxidation-reduction reaction under suitable experimental conditions. This is clearly shown by the following experiment (Fig. I, 28, 1). Solutions of stannous chloride and of ferric chloride, each acidified with dilute hydrochloric acid to increase the conductivity, are placed in separate beakers A and B, and the two solutions are connected by means of a "salt bridge" containing sodium chloride. The latter consists of an inverted U-tube filled with a solution of a conducting electrolyte, such as sodium chloride, and stoppered at each end with a plug of

\* It follows from Faraday's law that each gram equivalent weight of an ion is associated with a charge of one Faraday of electricity. A change of charge of one thus corresponds to the gain or loss of one Faraday per formula weight of the substance.

cotton wool to arrest mechanical flow. It connects the two parts of the redox system while preventing mixing. The electrolyte in solution in the salt bridge is always selected so that it does not react chemically with either of the solutions which it connects. Platinum foil electrodes are introduced into each of the solutions, and the two electrodes are connected to a millivoltmeter V. When the circuit is closed, it will be found that the current in the external circuit passes from the stannous chloride solution to the ferric chloride solution. After a little time, stannic ions can be detected in A and ferrous ions in B.

In the preceding experiment the flow of current is due to the e.m.f. produced by the chemical changes in the redox reaction. An electric current, according to modern theory, consists of a flow of electrons and it would therefore be expected to give rise to oxidation-reduction reactions. This can readily be demonstrated as follows. In Fig. I, 28, 1, beaker A contains ferrous ammonium sulphate solution acidified with dilute sulphuric acid, beaker B ferric chloride solution likewise acidified with dilute acid, and the salt bridge dilute sulphuric acid, and the millivoltmeter is replaced by a 6-volt battery with the positive pole connected to A and the negative pole to B. After some time ferric ions can be detected with potassium thiocyanate solution in A, and ferrous ions with potassium ferricyanide solution in B. At the anode (+ electrode) each ferrous ion loses one electron and becomes a ferric ion: at the cathode (— electrode) each ferric ion gains 1 electron and is reduced to a ferrous ion:



It is a well-known fact that oxidants and reductants vary considerably in strength. Information of a quantitative nature as to the relative strengths (compare relative strengths of weak acids and bases as expressed by their dissociation constants in Table I, 12, 1) would be of considerable practical value. A method which suggests itself at once is the measurement of the e.m.f. of redox reactions under standard conditions. This is indeed the method which is employed, but before this can be understood by the student, it will be necessary to consider the subject of electrode potentials.

**I, 29. Electrode Potentials.**—When a rod of zinc is partially immersed in a solution of zinc sulphate, the metal becomes negatively charged relative to the solution. To account for this, Nernst (1888) introduced the idea of **electrolytic solution pressure**. Just as a liquid passes into a vapour until the

pressure of the vapour has a definite value, so zinc when placed in a solution of one of its salts passes into solution as zinc ions. The zinc will consequently become negatively charged relative to the solution; a potential difference therefore exists between the metal and the solution. Owing to the comparatively large charge which the ions carry, the ions do not move far away from the metal but are held by electrostatic attraction and form an "electrical double layer." The electrolytic solution pressure  $P$  of the metal will be opposed by the osmotic pressure  $p$  of the ions in the solution, which tends to deposit them on the metal and the change soon stops (*i.e.* equilibrium is reached) when only a minute amount of zinc has passed into the ionic state. The greater the concentration of zinc in the solution, the greater is their osmotic pressure and the smaller is the negative potential of the zinc.

If a rod of copper (a metal with only a very small electrolytic solution pressure) is immersed in a solution of copper sulphate, a minute amount of copper ions deposits on the metal because of their osmotic pressure and the metal consequently acquires a positive charge, leaving the solution negatively charged.\* The metal then attracts negative ( $\text{SO}_4^{--}$ ) ions from the solution to form the "electrical double layer." The greater the concentration of copper ions in the solution, the larger is the osmotic pressure, and the greater is the positive potential of the copper.

The potential difference established between a metal and a solution of one of its salts, or the **electrode potential**, will be dependent upon the concentration of the ions of the metal in the solution and, of course, upon the metal itself. If  $P$  is the electrolytic solution pressure of the metal and  $p$  the osmotic pressure of the ions in the solution, we have: (a) if  $P > p$  (*e.g.* with zinc), the metal becomes negative in the solution; (b) if  $P < p$  (*e.g.* with copper or silver), the metal becomes positive in the solution; and (c) if  $P = p$ , the metal remains uncharged in the solution. The convention will be adopted in this book that the sign of the electrode potential is that of the metal: thus when the metal is positive with respect to the solution, it will be assumed to have a positive (+) potential. Other authors, particularly in the U.S.A., use the opposite algebraic sign.

\* Only in solutions in which the concentration, and therefore the osmotic pressure, of copper ions has been reduced to a very minute value (*e.g.* by the addition of excess of KCN and the formation of the complex ion  $[\text{Cu}(\text{CN})_4]^{--}$ ) does metallic copper send ions into the solution and so becomes negatively charged.

The electrodes just referred to are reversible with respect to the cation: one may also have electrodes which are reversible with respect to an anion. Thus when silver, in contact with solid silver chloride, is immersed in a solution of potassium chloride, that is, when one has the electrode  $\text{Ag}/\text{AgCl}$  (solid),  $\text{KCl}$ /, the potential will depend upon the concentration of the chloride ion, and the electrode will be reversible with reference to this ion. The calomel electrode, described in a later Section, is also reversible with respect to the anion.

Nernst (1889) deduced the following expression for computing the potential difference which exists between a metal and a solution of its ions, that is, for the electrode potential  $E$ :

$$E = \frac{RT}{nF} \log \frac{p}{P},$$

where  $R$  is the gas constant expressed in electrical units,  $F$  is the quantity of electricity borne by one equivalent weight in grams (one Faraday),  $n$  the valency of the ions and  $T$  the absolute temperature. The expression reduces to:

$$E_{18^\circ} = \frac{0.0577}{n} \log \frac{p}{P} \text{ volts, and } E_{25^\circ} = \frac{0.0591}{n} \log \frac{p}{P} \text{ volts}$$

at  $18^\circ\text{C}$  and  $25^\circ\text{C}$  respectively. The osmotic pressure  $p$  is directly proportional to the concentration of the solution and to the absolute temperature; the e.m.f. will therefore vary with the concentration. If the concentration is increased tenfold, the e.m.f. increases by 0.06 volt for a univalent ion, by  $0.06/2 = 0.03$  volt for a bivalent ion, etc. The electrolytic solution pressure provides a measure of the tendency of the metal to be converted into ions or, since the formation of ions constitutes an oxidation, it is also a measure of the capacity of the metal to undergo oxidation.

In order to determine the potential difference between an electrode and a solution, it is necessary to have another electrode and a solution, the potential difference between which is known. These two electrodes can then be combined to form a voltaic cell, the e.m.f. of which can be directly measured. The e.m.f. of the cell is the algebraic difference between the two electrode potentials; the value of the unknown potential can then be calculated. In practice the standard electrode used for comparative purposes is the **molar or normal hydrogen electrode**. This consists of a piece of platinum foil, coated with platinum black by an electrolytic process, and immersed in a solution of hydrochloric acid, molar with respect to

hydrogen ions (more correctly in a solution of hydrochloric acid containing hydrogen ions of unit activity). Hydrogen gas at a pressure of one atmosphere is passed over the foil through the side tube *C* (Fig. I, 29, 1) and escapes through the small openings *B* in the surrounding glass tube *A*; the foil is thus kept saturated with the gas. Connection between the platinum foil sealed into the tube *D* and an outer circuit is made with mercury in *D*. The platinum black has the remarkable property of adsorbing large quantities of hydrogen, and it permits the change from the gaseous to the ionic form and the reverse process to occur without hindrance; it therefore behaves as though it were composed entirely of hydrogen, that is, as a hydrogen electrode. Under fixed conditions, *viz.* of atmospheric pressure and molar concentration of hydrogen ions in

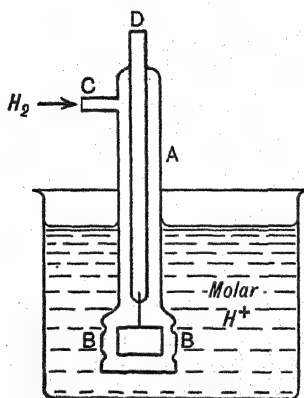
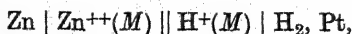


Fig. I, 29, 1

the solution in contact with the electrode, the hydrogen electrode possesses a definite potential at all temperatures. By connecting the molar hydrogen electrode with a metal electrode (a metal in contact with a molar solution of its ions) by means of a salt (say potassium chloride) bridge, the **molar or standard electrode potential** of the metal may be determined directly. Other electrodes, particularly the calomel electrode and the silver-silver chloride electrode, the potentials of which have been determined by direct reference to the molar

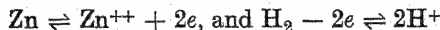
hydrogen electrode, are often used in practice owing to convenience of manipulation. The former is referred to again in Section I, 38, but for a fuller treatment the student is referred to text-books of physical chemistry.\*

When a rod of zinc is immersed in a molar solution of zinc ions and this is coupled with a molar hydrogen electrode, the resultant cell:



\* See, for example, S. Glasstone, *Text Book of Physical Chemistry*, Second Edition, 1947 (Macmillan). A detailed account is also to be found in the author's *Text-Book of Quantitative Inorganic Analysis: Theory and Practice*, Second Edition, 1951 (Longmans, Green & Co. Ltd.).

has an e.m.f. of 0.76 volt. The two reactions which take place are:



The zinc pole is negative and therefore the zinc electrode is 0.76 volt more negative than the hydrogen electrode, or the potential of the molar zinc electrode is -0.76 volt (the molar hydrogen electrode is arbitrarily taken as equal to zero). Further, if one employs a copper electrode immersed in a molar solution of cupric ions, and couples this with a molar hydrogen electrode, the cell has an e.m.f. of 0.34 volt. The copper pole is now positive; the potential of the molar copper electrode is accordingly +0.34 volt.

The **standard or molar electrode potential** of an element may therefore be defined as the e.m.f. produced when a half cell consisting of the element immersed in a molar solution of its ions (more correctly in a solution of its ions possessing unit activity) is coupled with a molar hydrogen electrode, the potential of which is assumed equal to zero. Table I, 29, 1 gives a list of standard electrode potentials at 25°C; the sign of the potential here adopted is that of the charge on the electrode.

TABLE I, 29, 1. STANDARD ELECTRODE POTENTIALS AT 25°C

Li/Li <sup>+</sup>	-3.045	Cr/Cr <sup>+++</sup>	-0.74
K/K <sup>+</sup>	-2.925	Fe/Fe <sup>++</sup>	-0.440
Na/Na <sup>+</sup>	-2.714	Cd/Cd <sup>++</sup>	-0.403
Ba/Ba <sup>++</sup>	-2.90	Co/Co <sup>++</sup>	-0.277
Sr/Sr <sup>++</sup>	-2.89	Ni/Ni <sup>++</sup>	-0.250
Ca/Ca <sup>++</sup>	-2.87	Sn/Sn <sup>++</sup>	-0.136
Ce/Ce <sup>+++</sup>	-2.48	Pb/Pb <sup>++</sup>	-0.126
Mg/Mg <sup>++</sup>	-2.37	Pt (H <sub>2</sub> )/H <sup>+</sup>	0.000
Th/Th <sup>++++</sup>	-1.90	Cu/Cu <sup>++</sup>	+0.337
Be/Be <sup>++</sup>	-1.85	2Hg/Hg <sub>2</sub> <sup>++</sup>	+0.789
V/V <sup>+++</sup>	-1.80	Ag/Ag <sup>+</sup>	+0.799
Al/Al <sup>+++</sup>	-1.66	Pd/Pd <sup>++</sup>	+0.99
Mn/Mn <sup>++</sup>	-1.18	Au/Au <sup>+++</sup>	+1.5
Zn/Zn <sup>++</sup>	-0.763		

When metals are arranged in the order of their standard electrode potentials, the so-called **electrochemical series** of the metals is obtained. The greater the negative value of the potential, the greater is the tendency of the metal to pass into the ionic state. A metal with a more negative potential will

displace any other metal below it in the series from solutions of its salts. Thus magnesium, aluminium, zinc or iron will displace copper from solutions of its salts; lead will displace copper, mercury or silver; copper will displace silver or mercury.

The standard electrode potential is a quantitative expression of the readiness of the element to lose electrons. It is therefore a measure of the strength of the element as a reducing agent; the more negative the element, the more powerful its action as a reductant.

**I, 30. Calculation of electrode potentials.**—The Nernst equation:

$$E = \frac{RT}{nF} \log_e \frac{p}{P}$$

may be written in the form:

$$E = \frac{RT}{nF} \log_e p - \frac{RT}{nF} \log_e P$$

At constant temperature the term  $\frac{RT}{nF} \log_e P$  is a constant for a given metal; hence:

$$E_+ = \frac{RT}{nF} \log_e p + \text{constant}$$

The gas laws may be written in the form  $p = RTc$  where  $c$  is the concentration of the positive ions in the solution. More accurately, the expression should be  $p = RTa_+$  where  $a_+$  is the activity of the ions.

Thus 
$$E_+ = \frac{RT}{nF} \log_e a_+ + \text{constant } (E_0)$$

The equation can be simplified by substituting the known values of the constants and converting the logarithms to base 10; it then becomes:

$$E_+ = \frac{0.0001982T}{n} \log a_+ + E_0$$

For a temperature of  $25^\circ\text{C}$  ( $T = 298^\circ$ ):

$$E_+ = \frac{0.0591}{n} \log a_+ + E_0 \quad (\text{i})$$

Before the introduction of the activity concept, the concentration of the ions  $c_{+}$  (in moles per litre) was used in place of the activity:

$$E_+ = \frac{0.0591}{n} \log c_{+} + E_0 \quad (\text{i}')$$



The latter expression is sufficiently accurate for most practical purposes in qualitative analysis.

For a non-metal, which yields negative ions, equation (i) becomes

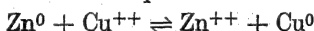
$$E_- = E_0 - \frac{0.0591}{n} \log a_-$$

where  $a_-$  is the activity of the negative ions. For purposes of calculation  $c_-$  may replace  $a_-$ .

It will be seen that for a solution of unit activity, where  $a_+$  or  $a_-$  is unity,  $E = E_0$ : thus  $E_0$  is the **standard or molar electrode potential** of the element. Knowing the value of  $E_0$ , the potential for any concentration can be calculated with the aid of equation (i').

An interesting application of this equation is to the calculation of equilibrium constants.

*Example 16.* Calculate the equilibrium constant of the reaction:



This is the familiar displacement of cupric ions from solutions by metallic zinc.

For the zinc electrode:

$$\begin{aligned} E_{\text{Zn}} &= E_0 + \frac{0.059}{2} \log [\text{Zn}^{++}], \\ &= -0.76 + 0.0295 \log [\text{Zn}^{++}] \end{aligned}$$

For the copper electrode:

$$\begin{aligned} E_{\text{Cu}} &= E_0 + \frac{0.059}{2} \log [\text{Cu}^{++}] \\ &= +0.34 + 0.0295 \log [\text{Cu}^{++}], \end{aligned}$$

At equilibrium  $E_{\text{Zn}} = E_{\text{Cu}}$

$$-0.76 + 0.0295 \log [\text{Zn}^{++}] = +0.34 + 0.0295 \log [\text{Cu}^{++}],$$

$$\text{or} \quad \log \frac{[\text{Zn}^{++}]}{[\text{Cu}^{++}]} = \frac{1.10}{0.0295} = 3.73,$$

$$\text{or} \quad \frac{[\text{Zn}^{++}]}{[\text{Cu}^{++}]} = 2 + 10^{3.7}$$

The equilibrium constant is given by:

$$\frac{[\text{Zn}^{++}] \times [\text{Cu}^0]}{[\text{Zn}^0] \times [\text{Cu}^{++}]} = K$$

Now  $[\text{Cu}^0]$  and  $[\text{Zn}^0]$  refer to the solid metallic condition and can therefore be regarded as constant quantities. The equation thus reduces to:

$$\frac{[\text{Zn}^{++}]}{[\text{Cu}^{++}]} = K'$$

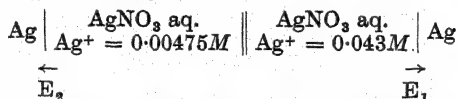
The ratio of the ionic concentrations at equilibrium is shown above to be  $2 \times 10^{37}$ , and this is the equilibrium constant of the reaction. In practice this means that when metallic zinc is added to a solution containing cupric ions, reaction ceases when the ratio of the concentration of the zinc ions produced to the concentration of the copper ions remaining in solution is  $2 \times 10^{37}$ , that is, a practically negligible quantity of cupric ions. For all ordinary purposes this may be taken as the complete removal of cupric ions from solution.

**I, 31. Concentration cells.**—The electrode potential varies with the concentration of the ions in solution. Hence by bringing two electrodes of the same metal but immersed in solutions containing different concentrations of the ions of the metal into contact, a cell may be formed. Such a cell is termed a **concentration cell**. The e.m.f. of the cell will be the algebraic difference of the two electrode potentials. It may be calculated as follows. At  $25^\circ$ :

$$E = \frac{0.0591}{n} \log c_1 + E_0 - \frac{0.0591}{n} \log c_2 - E_0,$$

$$= \frac{0.0591}{n} \log \frac{c_1}{c_2}, \text{ where } c_1 > c_2$$

As an example we may consider the cell:

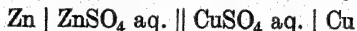


Assuming no potential difference at the liquid junction:

$$E = E_1 - E_2 = \frac{0.0591}{1} \log \frac{0.043}{0.00475} = 0.056 \text{ volt}$$

Concentration cells have an obvious application in the determination of the solubility of sparingly soluble salts.

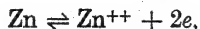
**I, 32. Calculation of the e.m.f. of a voltaic cell.**—One of the simplest of galvanic cells is the Daniell cell. This consists of a rod of zinc dipping in zinc sulphate solution and a strip of copper in copper sulphate solution; the two solutions are generally separated by placing one inside a porous pot and the other in the surrounding vessel. The cell may be represented:



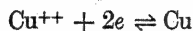
At the zinc electrode, zinc ions pass into solution leaving an equivalent negative charge on the metal. Copper ions are deposited at the copper electrode, rendering it positively charged. By completing the external circuit, the current

(electrons) passes from the zinc to the copper. The chemical reactions in the cell are as follows:

(a) zinc electrode—



(b) copper electrode—



The net chemical reaction is:



The potential difference at each electrode may be calculated by means of equation (i'), and the e.m.f. of the cell is the algebraic difference of the two potentials, the correct sign being applied to each.

As an example, we may calculate the e.m.f. of the Daniell cell with molar concentrations of zinc ions and cupric ions.

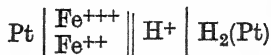
$$E = E_{0(\text{Cu})} - E_{0(\text{Zn})} = +0.344 - (-0.762) = 1.106 \text{ volts}$$

The small potential difference produced at the contact between the two solutions (the so-called liquid-junction potential) is neglected.

**I, 33. Oxidation-reduction cells.**—Reduction is accompanied by a gain of electrons and oxidation by a loss of electrons. In a system containing both an oxidising agent and its reduction product, there will be an equilibrium between them and electrons. If an inert electrode, such as platinum, is placed in a redox system, for example one containing ferric and ferrous ions, it will assume a definite potential indicative of the position of equilibrium. If the oxidation tendency predominates, the system will take electrons from the platinum leaving the latter positively charged; if, however, the system has reducing properties, electrons will be given up to the metal, which will then acquire a negative charge. The magnitude of the potential will thus be a measure of the oxidising or reducing power of the system.

To obtain comparative values of the "strengths" of oxidising agents it is necessary, as in the case of the electrode potentials of the metals, to measure under standard experimental conditions the potential difference between the platinum and the solution relative to a standard of reference. The primary standard is the molar or normal or standard hydrogen electrode, and its potential is taken as zero. The standard experimental conditions for the redox system are those in which the ratio of the concentrations of the oxidant to the reductant is unity.

Thus for a ferrous-ferric chloride electrode, the redox cell would be:



The potential measured in this way is called the **standard oxidation potential**. A selection of these is given in Table I, 33, 1. The sign of the potential is that of the electrode.

TABLE I, 33, 1. STANDARD OXIDATION POTENTIALS AT 25°C

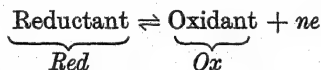
Electrode	Electrode reaction			E°
Co <sup>3+</sup> , Co <sup>2+</sup> /Pt	Co <sup>3+</sup>	+	e ⇌ Co <sup>2+</sup>	+1.84
Pb <sup>4+</sup> , Pb <sup>2+</sup> /Pt	Pb <sup>4+</sup>	+	2e ⇌ Pb <sup>2+</sup>	+1.75
MnO <sub>4</sub> <sup>-</sup> , MnO <sub>2</sub> /Pt	MnO <sub>4</sub> <sup>-</sup> + 4H <sup>+</sup>	+	3e ⇌ MnO <sub>2</sub> + 2H <sub>2</sub> O	+1.59
MnO <sub>4</sub> <sup>-</sup> , Mn <sup>2+</sup> /Pt	MnO <sub>4</sub> <sup>-</sup> + 8H <sup>+</sup>	+	5e ⇌ Mn <sup>2+</sup> + 4H <sub>2</sub> O	+1.51
Ce <sup>4+</sup> , Ce <sup>3+</sup> /Pt	Ce <sup>4+</sup>	+	e ⇌ Ce <sup>3+</sup>	+1.45
BrO <sub>3</sub> <sup>-</sup> , Br <sub>2</sub> /Pt	2BrO <sub>3</sub> <sup>-</sup> + 12H <sup>+</sup>	+	10e ⇌ Br <sub>2</sub> + 6H <sub>2</sub> O	+1.45
Cl <sub>2</sub> , 2Cl <sup>-</sup> /Pt	Cl <sub>2</sub>	+	2e ⇌ 2Cl <sup>-</sup>	+1.36
Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> , 2Cr <sup>3+</sup> /Pt	Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> + 14H <sup>+</sup>	+	6e ⇌ 2Cr <sup>3+</sup> + 7H <sub>2</sub> O	+1.36
IO <sub>3</sub> <sup>-</sup> , I <sub>2</sub> /Pt	2IO <sub>3</sub> <sup>-</sup> + 12H <sup>+</sup>	+	10e ⇌ I <sub>2</sub> + 6H <sub>2</sub> O	+1.20
Br <sub>2</sub> , 2Br <sup>-</sup> /Pt	Br <sub>2</sub>	+	2e ⇌ 2Br <sup>-</sup>	+1.07
Fe <sup>3+</sup> , Fe <sup>2+</sup> /Pt	Fe <sup>3+</sup>	+	e ⇌ Fe <sup>2+</sup>	+0.77
H <sub>3</sub> AsO <sub>4</sub> , H <sub>3</sub> AsO <sub>3</sub> /Pt	H <sub>3</sub> AsO <sub>4</sub> + 2H <sup>+</sup>	+	2e ⇌ H <sub>3</sub> AsO <sub>3</sub> + H <sub>2</sub> O	+0.56
I <sub>2</sub> , 2I <sup>-</sup> /Pt	I <sub>2</sub>	+	2e ⇌ 2I <sup>-</sup>	+0.53
[Fe(CN) <sub>6</sub> ] <sup>3-</sup> , [Fe(CN) <sub>6</sub> ] <sup>4-</sup> /Pt	Fe(CN) <sub>6</sub> <sup>3-</sup>	+	e ⇌ Fe(CN) <sub>6</sub> <sup>4-</sup>	+0.36
Cu <sup>2+</sup> , Cu/Pt	Cu <sup>2+</sup>	+	2e ⇌ Cu	+0.35
Sn <sup>4+</sup> , Sn <sup>2+</sup> /Pt	Sn <sup>4+</sup>	+	2e ⇌ Sn <sup>2+</sup>	+0.15
H <sup>+</sup> , H <sub>2</sub> /Pt	2H <sup>+</sup>	+	2e ⇌ H <sub>2</sub>	0.00
Ti <sup>4+</sup> , Ti <sup>3+</sup> /Pt	Ti <sup>4+</sup>	+	e ⇌ Ti <sup>3+</sup>	-0.04
Cr <sup>3+</sup> , Cr <sup>2+</sup> /Pt	Cr <sup>3+</sup>	+	e ⇌ Cr <sup>2+</sup>	-0.41
S <sup>0</sup> , S <sup>2-</sup> /Pt	S <sup>0</sup>	+	2e ⇌ S <sup>2-</sup>	-0.48
Zn <sup>2+</sup> , Zn	Zn <sup>2+</sup>	+	2e ⇌ Zn	-0.76

These oxidation potentials enable one to predict which ions will oxidise or reduce other ions at molar concentrations. The most powerful oxidising agents are at the upper end of the Table and the most powerful reducing agents at the lower end. Thus permanganate ions can oxidise Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, Fe<sup>2+</sup> and Fe(CN)<sub>6</sub><sup>3-</sup> ions; ferric ions can oxidise AsO<sub>3</sub><sup>3-</sup>, I<sup>-</sup>, but not Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> or Cl<sup>-</sup> ions. It must be emphasised that oxidation potentials do not give any information as to the velocity of the reaction; in some cases, the presence of a catalyst is necessary in order that the reaction may proceed with reasonable velocity.

In order to understand fully the significance of oxidation-reduction potentials and their application in calculations, it is advisable to consider that in all solutions of oxidants, some of the reduced form is always present: the concentration of the latter may

vary from a significant measurable quantity to an amount so small that it cannot be detected by any known method. A similar conception of reductants should be visualised. Thus in solutions containing ferric ion, there is always present some ferrous ion, and *vice versa*. In the quantitative study of oxidation-reduction reactions, both forms must always be considered, because, as we shall see in the following Section, it is their relative effective concentrations which determine the oxidising power or the oxidation potential of an oxidant. Examples of pairs include  $I_2, 2I^-$ ;  $MnO_4^-, Mn^{++}$ ;  $Fe^{+++}, Fe^{++}$ ; and  $Cr_2O_7^{--}, 2Cr^{+++}$ . When, therefore, we speak of the oxidant  $Cr_2O_7^{--}$ , the pair or system  $Cr_2O_7^{--}, 2Cr^{+++}$  is understood, notwithstanding the fact that chromic ion concentration may be infinitesimally small.

**I, 34. Calculation of the oxidation potential.**—A reversible oxidation-reduction reaction may be written in the form (oxidant = substance in oxidised state, reductant = substance in reduced state):



The electrode potential which is established when an inert or unattackable electrode is immersed in a solution containing both oxidant and reductant is given by the expression:

$$E_T = E^0 + \frac{RT}{nF} \log_e \frac{a_{Ox.}}{a_{Red.}} \quad (i)$$

where  $E_T$  is the observed potential of the redox electrode at  $T^\circ$ ,  $E^0$  is the standard oxidising potential,  $n$  the number of electrons or negative charges gained by the oxidant on being converted into the reductant, and  $a_{Ox.}$  and  $a_{Red.}$  are the activities of the oxidant and reductant respectively. Since activities are often difficult to determine directly, they may be replaced by concentrations; the error thereby introduced is usually of no great importance. The equation therefore becomes:

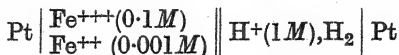
$$E_T = E^0 + \frac{RT}{nF} \log_e \frac{c_{Ox.}}{c_{Red.}} \quad (i')$$

Substituting the known values of  $R$  and  $F$ , and changing from natural logarithms to common or Briggsian logarithms (by multiplying by 2.303), we have for a temperature of  $25^\circ C$  ( $T = 298^\circ$ ):

$$E_{25} = E^0 + \frac{0.0591}{n} \log \frac{[Ox.]}{[Red.]} \quad (i'')$$

If the concentrations (or more accurately the activities) of the oxidant and reductant are equal,  $E_{25^\circ} = E^0$ , i.e. the standard oxidation potential. It follows from this expression that, for example, a tenfold change in the ratio of the concentrations of the oxidant to the reductant produces a change in the potential of the system of  $0.0591/n$  volts.

A simple example will illustrate the application of this formula. Consider the cell:

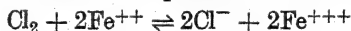


The e.m.f. is given by (the liquid junction potential between the acid and salt solutions is neglected):

$$\begin{aligned} E &= E^0 + \frac{0.0591}{1} \log \frac{[\text{Fe}^{+++}]}{[\text{Fe}^{++}]}; \\ &= +0.75 + 0.059 \log \frac{0.1}{0.001}; \\ &= +0.75 + 0.118 = 0.87 \text{ volt} \end{aligned}$$

The application of standard oxidation potentials to the calculation of equilibrium constants of simple ionic reactions is illustrated by the following example.

*Example 17.* Calculate the equilibrium constant of the reaction:



The equilibrium constant is given by:

$$\frac{[\text{Cl}^-]^2 \times [\text{Fe}^{+++}]^2}{[\text{Cl}_2] \times [\text{Fe}^{++}]^2} = K$$

The reaction may be regarded as taking place in a voltaic cell, the two half cells being a  $\text{Cl}_2, 2\text{Cl}^-$  electrode and a  $\text{Fe}^{++}, \text{Fe}^{+++}$  electrode. The reaction is allowed to proceed to equilibrium; the total voltage or e.m.f. of the cell will then be zero, i.e. the potentials of the two electrodes will be equal.

$$E^0_{\text{Cl}_2, 2\text{Cl}^-} + \frac{0.059}{2} \log \frac{[\text{Cl}_2]}{[\text{Cl}^-]^2} = E^0_{\text{Fe}^{++}, \text{Fe}^{+++}} + \frac{0.059}{1} \log \frac{[\text{Fe}^{+++}]}{[\text{Fe}^{++}]}$$

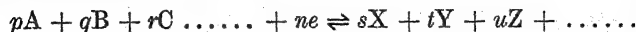
Now  $E^0_{\text{Cl}_2, 2\text{Cl}^-} = 1.36$  volts and  $E^0_{\text{Fe}^{++}, \text{Fe}^{+++}} = 0.77$  volt,

$$\therefore \log \frac{[\text{Fe}^{+++}]^2 \times [\text{Cl}^-]^2}{[\text{Fe}^{++}]^2 \times [\text{Cl}_2]} = \frac{0.59}{0.0295} = 20.00 = \log K,$$

$$K = 1.0 \times 10^{20}$$

The large value of the equilibrium constant signifies that the reaction will proceed from left to right almost to completion. This is in harmony with the practically complete oxidation of a ferrous salt by chlorine, and the stability of a ferric chloride solution.

**I, 35. Equilibrium Constant of Oxidation-Reduction Reactions.**—The general equation for an oxidation-reduction electrode may be written:



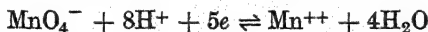
The potential is given by:

$$E = E^0 + \frac{RT}{nF} \log \frac{a_A^p \cdot a_B^q \cdot a_C^r \dots}{a_X^s \cdot a_Y^t \cdot a_Z^u \dots},$$

where  $a$  refers to activities, and  $n$  to the number of electrons involved in the oxidation-reduction reaction. This expression reduces to the following for a temperature of  $25^\circ\text{C}$  (concentrations are substituted for activities in order to permit of its facile application in practice):

$$E = E^0 + \frac{0.0591}{n} \log \frac{c_A^p \cdot c_B^q \cdot c_C^r \dots}{c_X^s \cdot c_Y^t \cdot c_Z^u \dots}.$$

It is, of course, possible to calculate the influence of change of concentration of certain constituents of the system by the use of the latter equation. Consider, for example, the permanganate reaction:



$$E = E^0 + \frac{0.0591}{5} \log \frac{[\text{MnO}_4^-] \times [\text{H}^+]^8}{[\text{Mn}^{++}]} \quad (\text{at } 25^\circ\text{C})$$

The concentration (or activity) of the water is taken as constant, since it is assumed that the reaction takes place in dilute solution, and the concentration of the water does not change appreciably as a result of the reaction. The equation may be written in the form:

$$E = E^0 + \frac{0.0591}{5} \log \frac{[\text{MnO}_4^-]}{[\text{Mn}^{++}]} + \frac{0.0591}{5} \log [\text{H}^+]^8$$

This enables one to calculate the effect of change in the ratio  $[\text{MnO}_4^-]/[\text{Mn}^{++}]$  at constant hydrogen ion concentration, or to compute the effect of change in the hydrogen ion concentration, other factors being maintained constant. In this particular case difficulties are experienced in the latter calculation owing to the fact that the reduction products of the permanganate ion vary at different hydrogen ion concentrations. In

\* More accurately, activities should be employed. The square brackets in heavy black (bold) type denote molecular concentrations.

other cases no such difficulties arise, and the calculation may be employed with confidence. Thus in the reaction:

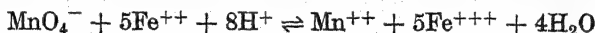


$$E = E^0 + \frac{0.0591}{2} \log \frac{[\text{H}_3\text{AsO}_4] \times [\text{H}^+]^2}{[\text{H}_3\text{AsO}_3]} \quad (\text{at } 25^\circ\text{C}),$$

$$\text{or} \quad E = E^0 + \frac{0.0591}{2} \log \frac{[\text{H}_3\text{AsO}_4]}{[\text{H}_3\text{AsO}_3]} + \frac{0.0591}{2} \log [\text{H}^+]^2$$

The calculation of equilibrium constants of more complex oxidation-reduction reactions (compare *Example 17*, Section I, 34) is best illustrated by an actual example.

*Example 18.* Calculate the equilibrium constant of the reaction:

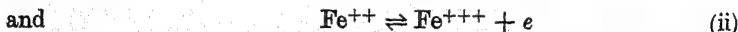
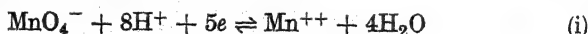


The equilibrium constant  $K$  is given by:

$$K = \frac{[\text{Mn}^{++}] \times [\text{Fe}^{+++}]^5}{[\text{MnO}_4^-] \times [\text{Fe}^{++}]^5 \times [\text{H}^+]^8}$$

The term  $4\text{H}_2\text{O}$  is omitted since the reaction is carried out in dilute solution and the water concentration may be assumed constant. The hydrogen ion concentration is taken as molar.

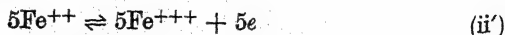
The complete reaction may be divided into two half-cell reactions corresponding to the partial equations:



For (i) as an oxidation-reduction electrode, one has:

$$\begin{aligned} E &= E^0 + \frac{0.059}{5} \log \frac{[\text{MnO}_4^-] \times [\text{H}^+]^8}{[\text{Mn}^{++}]} \\ &= 1.51 + \frac{0.059}{5} \log \frac{[\text{MnO}_4^-] \times [\text{H}^+]^8}{[\text{Mn}^{++}]} \end{aligned}$$

The partial ionic equation (ii) may be multiplied by 5 in order to balance (i) electrically:



For (ii') as an oxidation-reduction electrode:

$$\begin{aligned} E &= E^0 + \frac{0.059}{5} \log \frac{[\text{Fe}^{+++}]^5}{[\text{Fe}^{++}]^5}, \\ &= 0.77 + \frac{0.059}{5} \log \frac{[\text{Fe}^{+++}]^5}{[\text{Fe}^{++}]^5} \end{aligned}$$



Combining the two electrodes into a cell, the e.m.f. will be zero when equilibrium is attained:

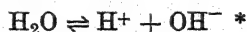
$$\text{i.e. } 1.51 + \frac{0.059}{5} \log \frac{[\text{MnO}_4^-] \times [\text{H}^+]^8}{[\text{Mn}^{++}]} = 0.77 + \frac{0.059}{5} \log \frac{[\text{Fe}^{+++}]^5}{[\text{Fe}^{++}]^5},$$

$$\text{or } \log \frac{[\text{Mn}^{++}] \times [\text{Fe}^{+++}]^5}{[\text{MnO}_4^-] \times [\text{Fe}^{++}]^5 \times [\text{H}^+]^8} = \frac{5(1.51 - 0.77)}{0.059} = 62.7$$

$$K = \frac{[\text{Mn}^{++}] \times [\text{Fe}^{+++}]^5}{[\text{MnO}_4^-] \times [\text{Fe}^{++}]^5 \times [\text{H}^+]^8} = 8.5 \times 10^{62}$$

This result clearly indicates that the reaction proceeds to completion.

**I, 36. The Ionic Product of Water.**—Kohlrausch and Heidweiller (1894) found that the most highly purified water that can be obtained possesses a small but definite electrical conductivity. Water must therefore be slightly ionised in accordance with the equation:



Applying the law of mass action to this equation, one obtains, for any fixed temperature:

$$\frac{a_{\text{H}^+} \times a_{\text{OH}^-}}{a_{\text{H}_2\text{O}}} = \frac{[\text{H}^+] \cdot [\text{OH}^-]}{[\text{H}_2\text{O}]} \times \frac{f_{\text{H}^+} \cdot f_{\text{OH}^-}}{f_{\text{H}_2\text{O}}} = \text{a constant},$$

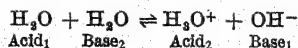
where  $a_x$ ,  $[x]$ , and  $f_x$  refer to the activity, concentration and activity coefficient respectively of the species  $x$ . Since water is only slightly ionised, the ionic concentrations will be small and their activity coefficients may be regarded as unity; the activity coefficient of the unionised molecules may also be taken as unity. The expression thus becomes:

$$\frac{[\text{H}^+] \times [\text{OH}^-]}{[\text{H}_2\text{O}]} = \text{a constant}$$

\* Strictly speaking the hydrogen ion exists in water as the hydroxonium ion  $\text{H}_3\text{O}^+$ . The electrolytic dissociation of water should therefore be written:



On the Lowry-Brønsted hypothesis, water may be regarded as undergoing ionisation as an acid donating a proton to another molecule of water functioning as a base:



For the sake of simplicity, the more familiar symbol  $\text{H}^+$  will be retained, particularly as in the subsequent discussion the term  $p\text{H}$  and not  $p(\text{H}_3\text{O})$  is employed.

In pure water or in dilute aqueous solutions, the concentration of the undissociated water may be considered constant. Hence:

$$[\text{H}^+] \times [\text{OH}^-] = K_w$$

$K_w$  is the ionic product of water. It must be pointed out that the assumption that the activity coefficients of the ions are unity and that the activity coefficient of water is constant applies strictly to pure water and to very dilute solutions (ionic strength  $> 0.01$ ); in more concentrated solutions, *i.e.* in solutions of appreciable ionic strength, the electrical environment affects the activity coefficients of the ions and also the activity of the unionised water. The ionic product of water will then not be constant, but will depend upon the ionic environment. It is, however, difficult to determine the activity coefficients, except under specially selected conditions, so that in practice the ionic product  $K_w$ , although not strictly constant, is employed.

The ionic product varies with the temperature, but under ordinary experimental conditions (at about  $25^\circ$ ) its value may be taken as  $1 \times 10^{-14}$  with concentrations expressed in gram ions per litre. This is sensibly constant in dilute aqueous solution. If the product of  $[\text{H}^+]$  and  $[\text{OH}^-]$  in aqueous solution momentarily exceeds this value, the excess ions will immediately combine to form water. Similarly, if the product of the two ionic concentrations is momentarily less than  $10^{-14}$ , more water molecules will dissociate until the equilibrium value is attained.

The hydrogen and hydroxyl ion concentrations are equal in pure water; therefore:

$$[\text{H}^+] = [\text{OH}^-] = \sqrt{K_w} = 10^{-7} \text{ gram ions per litre at about } 25^\circ$$

A solution in which the hydrogen and hydroxyl ion concentrations are equal is termed an exactly **neutral solution**. If  $[\text{H}^+]$  is greater than  $10^{-7}$ , the solution is **acid**, and if less than  $10^{-7}$ , the solution is **alkaline** (or basic). It follows that at ordinary temperatures  $[\text{OH}^-]$  is greater than  $10^{-7}$  in alkaline solution and less than this value in acid solution.

In all cases the reaction of the solution can be quantitatively expressed by the magnitude of the hydrogen ion (or hydroxonium ion) concentration, or less frequently of the hydroxyl ion concentration, since the following simple relations between  $[\text{H}^+]$  and  $[\text{OH}^-]$  exist:

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]}, \text{ and } [\text{OH}^-] = \frac{K_w}{[\text{H}^+]}$$

The variation of  $K_w$  with temperature is shown in Table I, 36, 1.

TABLE I, 36, 1. IONIC PRODUCT OF WATER AT VARIOUS TEMPERATURES

Temp. (°C)	$K_w \times 10^{-14}$	Temp. (°C)	$K_w \times 10^{-14}$
0°	0.12	35°	2.09
5°	0.19	40°	2.92
10°	0.29	45°	4.02
15°	0.45	50°	5.48
20°	0.68	55°	7.30
25°	1.01	60°	9.62
30°	1.47		

**I, 37. Hydrogen Ion Exponent ( $pH$ ).—**For many purposes, especially when dealing with small concentrations, it is cumbersome to express concentrations of hydrogen and of hydroxyl ions in terms of gram equivalents per litre. A very convenient method was proposed by Sørensen (1909). He introduced the **hydrogen ion exponent  $pH$**  defined by the relationships:

$$pH = -\log_{10} [H^+] = \log \frac{1}{[H^+]}, \text{ or } [H^+] = 10^{-pH}$$

The quantity  $pH$  is thus the logarithm of the reciprocal of the hydrogen ion concentration, or is equal to the logarithm of the hydrogen ion concentration with negative sign.\* This method has the advantage that all states of acidity and alkalinity between those of solutions molar (or normal) with respect to hydrogen or hydroxyl ions, can be expressed by a series of positive numbers between 0 and 14. Thus a neutral solution with  $[H^+] = 10^{-7}$  has a  $pH$  of 7; a solution with a molar (or normal) concentration of hydrogen ions has a  $pH$  of 0 ( $= 10^0$ ); and a solution molar with respect to hydroxyl ions has  $[H^+] = K_w / [OH^-] = 10^{-14}/10^0 = 10^{-14}$  and possesses a  $pH$  of 14. A neutral solution is therefore one in which  $pH = 7$ , an acid solution one in which  $pH < 7$ , and an alkaline solution one in which  $pH > 7$ . The greater the hydrogen ion concentration, the smaller is the  $pH$ . An alternative definition for a neutral

\* Strictly speaking  $pH$  should be defined in terms of activity, *i.e.*

$$pH = -\log a_{H^+} \text{ or } a_{H^+} = 10^{-pH}$$

Because of uncertainties relating to single ion activities, it is usual in approximate calculations to employ the concentration rather than the activity of the hydrogen ion when defining  $pH$ . Similar remarks apply to  $pOH$ .

solution is one in which the hydrogen ion and hydroxyl ion concentrations are equal. In an acid solution the hydrogen ion concentration exceeds the hydroxyl ion concentration, whilst in an alkaline or basic solution the hydroxyl ion concentration is the greater.

*Examples.*—(i) Find the  $pH$  of a solution of which  $[H^+] = 4.0 \times 10^{-5}$ .

$\log 4.0 = 0.602$ , hence  $\log 4.0 \times 10^{-5}$  is

$$\bar{5}.602 = 0.602 - 5 = -4.398$$

(the decimal part or mantissa of the logarithm is always positive).

$$pH = -\log [H^+] = -(-4.398) = 4.398$$

(ii) Find the hydrogen ion concentration corresponding to  $pH = 5.643$ .

$$pH = -\log [H^+] = 5.643; \therefore \log [H^+] = -5.643$$

This must be written in the usual form containing a negative characteristic and a positive mantissa:

$$\log [H^+] = -5.643 = \bar{6}.357$$

Referring to a table of antilogarithms, the number corresponding to the logarithm 0.357 is 2.28; the number corresponding to the logarithm  $\bar{6}.357$  is accordingly  $2.28 \times 10^{-6}$ .

$$[H^+] \text{ is therefore } 2.28 \times 10^{-6}$$

(iii) Calculate the  $pH$  of a 0.01 molar solution of acetic acid (the degree of dissociation is 12.5 per cent).

The hydrogen ion concentration is  $0.125 \times 0.01 = 1.25 \times 10^{-3}$ .  
Now  $\log 1.25 = 0.097$ ;

$$\therefore pH = -(-3 + 0.097) = 2.903$$

The hydroxyl ion concentration may be expressed in a similar way:

$$pOH = -\log_{10} [OH^-] = \log \frac{1}{[OH^-]}, \text{ or } [OH^-] = 10^{-pOH}$$

If one writes the equation:

$$[H^+] \times [OH^-] = K_w = 10^{-14},$$

in the form:

$$\log [H^+] + \log [OH^-] = \log K_w = -14$$

$$\text{then } pH + pOH = pK_w = 14.$$

This relationship should hold for all dilute solutions at about  $25^\circ$ .

Fig. I, 37, 1 will serve as a useful mnemonic for the relation between  $[H^+]$ ,  $pH$ ,  $[OH^-]$  and  $pOH$  in acid and alkaline solution.

The logarithmic or exponential method has also been found useful for expressing other small numerical quantities which arise in qualitative analysis. These include (i) dissociation

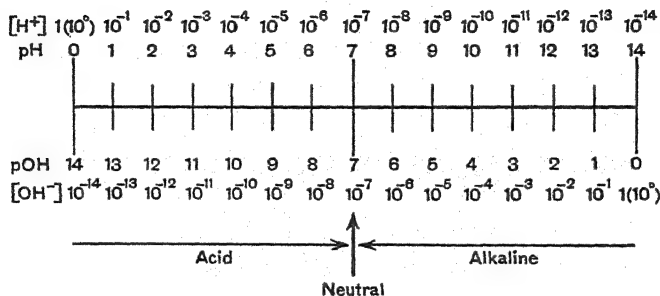


Fig. I, 37, 1

constants, (ii) other ionic concentrations, and (iii) solubility products.

(i) For any acid with a dissociation constant of  $K_a$ :

$$pK_a = -\log K_a = \log \frac{1}{K_a}$$

Similarly for any base with dissociation constant  $K_b$ :

$$pK_b = -\log K_b = \log \frac{1}{K_b}$$

(ii) For any ion I of concentration  $[I]$ :

$$pI = -\log [I] = \log \frac{1}{[I]}$$

Thus for

$$[Na^+] = 8 \times 10^{-5}, pNa = 4.1$$

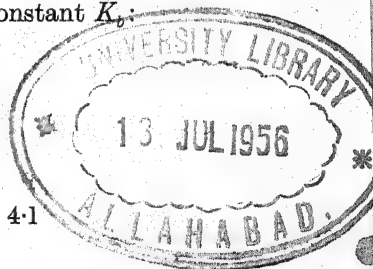
(iii) For a salt with solubility product S:

$$pS = -\log S = \log \frac{1}{S}$$

### I, 38. Determination of the Hydrogen Ion Concentration.

—The hydrogen ion concentration of a solution is of great importance both in pure and in applied chemistry. Two methods are commonly employed for its estimation, (a) the colorimetric method and (b) the electrometric method.

**The Colorimetric Method.** In this method one employs what are known as indicators. An indicator is a substance



which varies in colour according to the hydrogen ion concentration. It is generally a weak organic acid or base and is employed in very dilute solution. The change in colour is usually due either to the production of different tautomeric forms of the original substance or to the formation of coloured ions; the formation of these takes place over a small but definite  $pH$  range. The hydrogen ion concentrations at which different indicators exhibit their colour change have been determined by direct electrometric methods; the  $pH$  range over which the indicator is applicable is thus known. Table I, 38, 1 summarises the  $pH$  values of a number of the more common indicators.

There are two methods for the determination of the  $pH$  of a solution colorimetrically.

**A. Buffer Solution Method.** The approximate  $pH$  of the solution must be found first with the aid of a multiple-range indicator solution (for example, the B.D.H. "universal" indicator\*), by the systematic use of a number of indicators, or by the use of indicator test papers.† A "wide range" or "universal" test paper, covering  $pH$  1–2 to 10, is marketed, as well as a number of "narrow range" indicator test papers which cover most of the  $pH$  range in steps of 1.5–2  $pH$  units. Colour-matching charts are supplied by the manufacturers to show the change in colour at 0.3  $pH$  intervals. The test papers are best used, and their accuracy is greatest, by dipping the papers into the fluid: if the test solution is "spotted" on the indicator paper the colour shade of the spot produced may vary from the centre outwards and some difficulty may be experienced in deciding which shade to consider as showing the actual  $pH$ . The test papers tend to deteriorate with storage. For the average observer, it is doubtful whether the test papers permit the determination of  $pH$  closer than to 0.5–1  $pH$  unit, but this suffices for many purposes.

A series of buffer solutions (Sections I, 39 and A, 4) is selected, differing successively in  $pH$  by about 0.2, covering the  $pH$

\* A "universal" indicator may be prepared, after Bogen, by dissolving 0.2 g. of phenolphthalein, 0.4 g. of methyl red, 0.6 g. of dimethylaminoazobenzene, 0.8 g. of bromothymol blue and 1.0 g. of thymol blue in 1 litre of absolute ethyl alcohol. Dilute sodium hydroxide solution is added dropwise until the colour changes to the yellow corresponding to the neutral region. The colours over the  $pH$  scale are:

$pH$	2	4	6	8	10	12
Colour	red	orange	yellow	green	blue	purple

† Manufactured in Great Britain by British Drug Houses Ltd., Poole, Dorset, and by Johnsons of Hendon Ltd., Hendon Way, London, N.W.4. Equivalent test papers are available in the U.S.A.

range of the solutions under investigation; the range of buffer solutions required will be indicated by the preliminary *pH*

TABLE I, 38, 1. COLOUR CHANGES AND *pH* RANGE OF SOME INDICATORS

<i>Indicator</i>	<i>Chemical name</i>	<i>Colour in acid solution</i>	<i>Colour in alkaline solution</i>	<i>pH range</i>
Brilliant cresyl blue (acid)	Amino-diethylamino-methyl diphenazonium chloride	Red-orange	Blue	0.0-1.0
$\alpha$ -Naphthol-benzen (acid)		Colourless	Yellow	0.0-0.8
Methyl violet	Pentamethyl <i>p</i> -rosaniline hydrochloride	Yellow	Blue-green	0.0-1.8
Cresol red (acid)	<i>o</i> -Cresolsulphone-phthalein	Red	Yellow	1.2-2.8
Thymol blue (acid)	Thymol-sulphone-phthalein	Red	Yellow	1.2-2.8
Meta cresol purple	<i>m</i> -Cresolsulphone-phthalein	Red	Yellow	1.2-2.8
Bromo-phenol blue	Tetrabromophenol-sulphone phthalein	Yellow	Blue	2.8-4.6
Methyl orange	Dimethylamino-azo-benzene-sodium sulphonate	Red	Yellow	3.1-4.4
Congo red	Diphenyl-bis-azo- $\alpha$ -naphthylamine-4-sulphonic acid	Violet	Red	3.0-5.0
Bromo-cresol green	Tetrabromo- <i>m</i> -cresol-sulphone-phthalein	Yellow	Blue	3.8-5.4
Methyl red	<i>o</i> -Carboxybenzene-azo-dimethylaniline	Red	Yellow	4.2-6.3
Chloro-phenol red	Dichlorophenol-sulphone-phthalein	Yellow	Red	4.8-6.4
Azolitmin (litmus)		Red	Blue	5.0-8.0
Bromo-thymol blue	Dibromo-thymol-sulphone-phthalein	Yellow	Blue	6.0-7.6
Diphenol purple	<i>o</i> -Hydroxy-diphenyl-sulphone-phthalein	Yellow	Violet	7.0-8.6
Cresol red (base)	<i>o</i> -Cresol-sulphone-phthalein	Yellow	Red	7.2-8.8
$\alpha$ -Naphthol-phthalein	$\alpha$ -Naphthol-phthalein	Yellow	Blue	7.3-8.7
Thymol blue (base)	Thymol-sulphone-phthalein	Yellow	Blue	8.0-9.6
$\alpha$ -Naphthol-benzen (base)		Yellow	Blue-green	8.2-10.0
Phenol-phthalein	Phenol-phthalein	Colourless	Red	8.3-10.0
Thymol-phthalein	Thymol-phthalein	Colourless	Blue	9.3-10.5
Brilliant cresyl blue (base)	(See above)	Blue	Yellow	10.8-12.0

determination. Equal volumes, say 5 or 10 ml., of the buffer solutions differing successively in  $pH$  by about 0.2 are placed in test-tubes of colourless glass and having approximately the same dimensions, and a small quantity of a suitable indicator for the particular  $pH$  range is added to each tube. A series of different colours corresponding to the different  $pH$  values is thus obtained. An equal volume (say 5 or 10 ml.) of the test solution is treated with an equal volume of indicator to that used for the buffer solutions, and the resulting colour is compared with that of the individual coloured, standard buffer solutions. When a complete (or almost complete) match is found, the test solution and the corresponding buffer solution

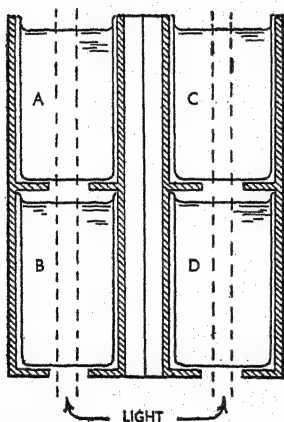


Fig. I, 38, 1

have the same  $pH$  within 0.2  $pH$  unit. For matching the colours, the buffer solutions may be arranged in the holes of a test-tube stand in order of increasing  $pH$ ; the test solution is then moved from hole to hole until the best colour match is obtained. Special stands and standards for making the comparison are available commercially (e.g. from The British Drug Houses Ltd.). The commercial standards, prepared from buffer solutions, are not permanent and must be checked every six months.

For turbid or slightly coloured solutions, the direct-comparison method given above can no longer be applied. The interference due to the coloured substance can be eliminated in a simple way by a device due to H. Walpole (1916). In Fig. I, 38, 1, A, B, C and D are glass cylinders with plain bottoms standing in a box, which is painted dull black on the inside. A contains the coloured solution to be tested (here the test solution + indicator), B contains an equal volume of water, C contains a solution of known strength for comparison (here the standard buffer solution + indicator), whilst D contains the same volume of the solution to be tested as was originally added to A. The colour of the unknown solution is thus compensated for.

**B. Comparator (or Permanent Colour Standard) Method.** In this procedure comparison is made with a series of permanent glass colour standards. Nine glass colour standards



are fitted into a disc, and the latter is inserted into a **comparator**, which is furnished with four compartments to receive small test-tubes or rectangular glass cells, and is also provided with an opal glass screen. The disc can revolve in the comparator, and each colour standard passes in turn in front of an aperture through which the solution in the cell (or cells) can be observed. As the disc revolves, the *pH* value of the colour standard visible in the aperture appears in a special recess. The **Lovibond comparator\*** is shown in Fig. I, 38, 2: this may be used with 13.5 mm. test-tubes or 13.5 mm. rectangular cells. The comparator is employed with B.D.H. indicators. The colour discs available include cresol red (acid and base range) thymol blue (acid and base range), bromophenol blue, bromocresol

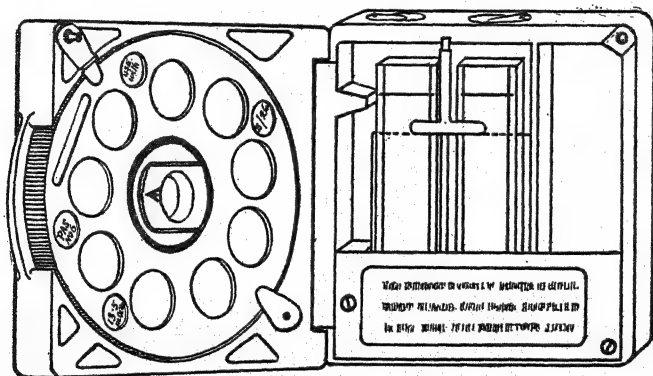


Fig. I, 38, 2

blue, bromocresol green, methyl red, chlorophenol red, bromocresol purple, bromothymol blue, phenol red, diphenol purple, cresol red, thymol blue and the B.D.H. "universal" indicator—the *pH* ranges for these indicators are given in Table I, 38, 1.

A determination of the approximate *pH* of the solution is first made with a "universal" or "wide range" indicator or with indicator test papers (see under A), and then a suitable disc is selected. Ten ml. of the unknown solution is placed in the glass test-tube or cell, the appropriate quantity of indicator (usually 0.5 ml.) is added, and the colour is matched against the glass disc. Provision is made in the apparatus for

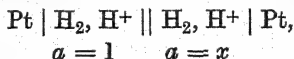
\* Manufactured by The Tintometer Ltd., Milford, Salisbury, England. A similar apparatus is marketed by Hellige, Inc., of Long Island City 1, N.Y., U.S.A.: this utilises Merck's (U.S.A.) indicators. The glass discs in the two instruments are not interchangeable.

the application of the Walpole technique—by the insertion of a “blank” containing the solution. It is claimed that results accurate to 0.2 pH unit can be obtained.

**The Electrometric Method.** The e.m.f. of a concentration cell at 25° is given by (Section I, 31):

$$E = \frac{0.0591}{n} \log \frac{c_1}{c_2}$$

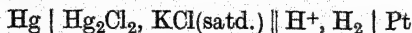
If a hydrogen electrode (Section I, 29) is immersed in the solution the pH of which is to be measured, and this half cell coupled with a molar (or normal) hydrogen electrode by means of a potassium chloride solution bridge in order to eliminate liquid junction potential, the e.m.f. of the resulting cell:



may be measured.

$$\begin{aligned} \text{Here} \quad E &= \frac{0.0591}{1} \log \frac{1}{[\text{H}^+]} \text{ (at ca. 25°),} \\ &= 0.0591 \text{ pH} \\ \therefore \text{pH} &= E/0.0591 \end{aligned}$$

The use of the molar hydrogen electrode as a standard electrode or half cell presents certain practical difficulties. It is usual to employ some form of the calomel electrode as a secondary standard half cell. A **calomel electrode** is one in which mercury and calomel are covered with a potassium chloride solution of definite concentration; this may be 0.1*N*, *N*, 3.5*N* or saturated. The potassium chloride solution must be saturated with calomel. The potential of, say, the saturated calomel electrode (*i.e.* that prepared with saturated potassium chloride solution) must first be determined with reference to the molar hydrogen electrode. Let this value be designated  $E_{\text{cal. (sat.)}}$ . For the measurement of hydrogen ion concentration one then employs the cell:



Let the resultant e.m.f. be  $E_{\text{obs.}}$ . One then has at 25°:

$$\begin{aligned} E_{\text{obs.}} &= E_{\text{cal. (sat.)}} - 0.0591 \log [\text{H}^+], \\ \text{pH} &= \frac{E_{\text{obs.}} - E_{\text{cal. (sat.)}}}{0.0591} \end{aligned}$$

The value of  $E_{\text{cal. (sat.)}}$  is 0.246 volt at 25°. The corresponding figures (at 25°) for the decinormal and normal calomel electrodes are 0.337 and 0.285 volt respectively.

A simple form of calomel electrode suitable for elementary work is illustrated in Fig. 1, 38, 3. It consists of a glass vessel provided with a bent side tube A and another side tube B, over the end of which a piece of rubber tubing is placed which can be closed by a spring or screw clip. Electrical connexion with the electrode is made by means of a platinum wire, sealed through a glass tube C; the latter contains a little pure mercury into which an amalgamated copper wire dips. To set up the electrode a saturated solution of analytically pure potassium chloride containing some solid salt is first prepared. Pure mercury to a depth of about 0.5 cm. is placed in the bottom of the dry electrode vessel; the mercury is then covered with a layer of calomel paste. The latter is prepared by rubbing pure calomel, mercury and saturated potassium chloride solution together in a mortar; the supernatant liquid is poured off and the rubbing process repeated twice with fresh quantities of saturated potassium chloride solution. The rubber stopper carrying the glass tube and platinum wire is then inserted, care being taken that the platinum wire dips into the mercury. The vessel is then filled with a saturated solution of potassium chloride (previously saturated with calomel by shaking with the solid salt) by drawing in the solution through the bent tube A and then closing the rubber tube B with a clip. The electrode is then ready for use.

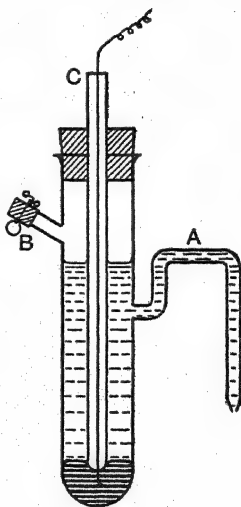
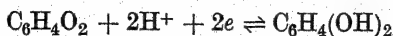


Fig. 1, 38, 3

The preparation of reproducible hydrogen electrodes is a comparatively tedious process. The electrode cannot be employed in the presence of reducible substances or of ions which have positive electrode potentials (see Table I, 33, 1), such as copper, silver and gold. Büllmann (1921) introduced the **quinhydrone electrode**; this renders the determination of *pH* a rapid and simple process and does not involve the use of hydrogen gas. The underlying theory is as follows. Let us consider the reversible reduction of quinone to quinhydrone in acid solution:



This is a reversible oxidation-reduction system and the potential

of an inert electrode, such as platinum, immersed in the system is given by:

$$\begin{aligned} E &= E^0 + \frac{RT}{2F} \log_e \frac{a_Q \cdot a_{H^+}}{a_{H_2Q}}, \\ &= E^0 + \frac{RT}{2F} \log_e \frac{a_Q}{a_{H_2Q}} + \frac{RT}{F} \log_e a_{H^+}, \end{aligned}$$

where  $a_Q$ ,  $a_{H^+}$ ,  $a_{H_2Q}$  are the activities of the quinone, hydrogen ions and hydroquinone respectively, and  $E^0$  is the standard potential referred to the molar hydrogen electrode. If the solution contains equi-molecular amounts of quinone and hydroquinone, the ratio of the activities may be regarded as unity:

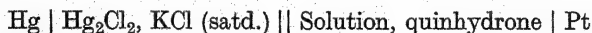
$$E = E^0 + \frac{RT}{F} \log_e a_{H^+} \quad (i)$$

The sparingly soluble substance quinhydrone is a molecular compound of quinone and hydroquinone,  $C_6H_4O_2 \cdot C_6H_4(OH)_2$ , and dissociates into the two components when dissolved in water; it follows, therefore, that in the pH range over which this compound is stable, equation (i) holds. It may therefore be employed for the determination of pH.  $E^0$  has been determined in the usual manner by direct reference to the molar (or normal) hydrogen electrode, and has a value of 0.704 volt at 18° and 0.699 volt at 25°. By making the usual substitution for the known values of the constants in equation (i), one obtains at 25°:

$$E = 0.699 + 0.0591 \log a_{H^+}$$

Thus the potential of the quinhydrone electrode changes with the hydrogen ion activity in a manner which is exactly similar to that of the hydrogen electrode.

To determine the pH of a solution, the quinhydrone electrode may be combined with a calomel electrode, thus forming the cell:



The potential of the saturated calomel electrode,  $E_{\text{cal. (sat.)}}$ , against the molar hydrogen electrode is 0.246 volt at 25°.

Hence

$$\begin{aligned} E_{\text{obs.}} &= E_{\text{quinhydrone}} - E_{\text{cal. (sat.)}} \\ &= 0.699 + 0.0591 \log [H^+] - 0.246 \\ &= 0.453 + 0.0591 \log [H^+] \end{aligned}$$

$$-\log [H^+] = \text{pH} = \frac{0.453 - E_{\text{obs.}}}{0.0591}$$

To carry out the determination of the hydrogen ion concentration of a solution, about 1 gram of quinhydrone per 100 ml. of the solution is added, and the solution stirred. A bright platinum electrode is immersed in the solution and the quinhydrone electrode combined in a cell with a saturated calomel electrode; a saturated solution of potassium chloride may be used as the salt bridge. The e.m.f. of the cell is determined and the  $pH$  calculated. The e.m.f. is measured by the potentiometer method based upon the Poggendorff compensation principle; details of this will be found in text-books of physical chemistry\*. It must be pointed out that the quinhydrone electrode cannot be employed in alkaline solutions in which the  $pH$  is greater than 8, for the ratio of quinone to hydroquinone is no longer unity†.

Determinations of  $pH$  can be rapidly made with the aid of a glass electrode and a  $pH$  meter: a description of these is outside the scope of this volume.\*

**I, 39. Buffer Solutions.**—A solution of 0.0001M hydrochloric acid should give a  $pH$  equal to 4, but the solution is extremely sensitive to traces of alkali from the glass of the containing vessel and to ammonia from the air. Likewise a 0.0001M solution of sodium hydroxide, which should have a  $pH$  of 10, is sensitive to traces of carbon dioxide from the atmosphere. Aqueous solutions of potassium chloride and of ammonium acetate have a  $pH$  of about 7. The addition of 1 ml. of molar hydrochloric acid to 1 litre of the solution results in a change of  $pH$  to 3 in the former case and in very little change in the latter. ✓ The resistance of a solution to changes in hydrogen ion concentration upon the addition of acid or alkali is termed **buffer action**; a solution which possesses such properties is known as a **buffer solution**. It is said to possess "reserve acidity" and "reserve alkalinity." Solutions of which the  $pH$  values (determined by reference to the hydrogen electrode) are known, which can be readily prepared and which are unaffected by small additions of alkali or acid, are required for the colorimetric determination of hydrogen ion concentration and for other purposes.

Buffer mixtures usually consist of solutions containing a mixture of a weak acid or base and its salt. In order to

\* A detailed account is also given in the author's *Text Book of Quantitative Inorganic Analysis: Theory and Practice*, Second Edition, 1951 (Longmans, Green & Co. Ltd.).

† This is partly due to the facile oxidation of hydroquinone in alkaline solution and partly to the ionisation of hydroquinone as a weak dibasic acid. The effect of the latter is reduced in buffered solutions.

understand buffer action, let us study first the equilibrium between a weak acid and its salt. The dissociation of a weak acid HA is given by:



and its magnitude is controlled by the value of the dissociation constant  $K_a$ :

$$\frac{a_{\text{H}^+} \times a_{\text{A}^-}}{a_{\text{HA}}} = K_a, \quad \text{or} \quad a_{\text{H}^+} = \frac{a_{\text{HA}}}{a_{\text{A}^-}} \times K_a \quad (\text{i})$$

where  $a_x$  refers to the activity of the species X. The expression may be approximated by writing concentrations for activities (strictly speaking, it will be recalled (Section I, 11), activity = concentration  $\times$  activity coefficient):

$$[\text{H}^+] = \frac{[\text{HA}]}{[\text{A}^-]} \times K_a \quad (\text{ii})$$

This equilibrium applies to a mixture of an acid HA and its salt, say, MA. If the concentration of the acid be  $c_a$  and that of the salt be  $c_s$ , then the concentration of the undissociated portion of the acid is  $c_a - [\text{H}^+]$ . The solution is electrically neutral, hence  $[\text{A}^-] = c_s + [\text{H}^+]$  (the salt is completely dissociated). Substituting these values in the equilibrium equation (ii):

$$[\text{H}^+] = \frac{c_a - [\text{H}^+]}{c_s + [\text{H}^+]} \times K_a \quad (\text{iii})$$

This is a quadratic equation for  $[\text{H}^+]$ , and may be solved in the usual manner. It can, however, be simplified by introducing the following approximation. In a mixture of a weak acid and its salt, the dissociation of the acid is repressed by the common ion effect, and  $[\text{H}^+]$  may be taken as negligibly small by comparison with  $c_a$  and  $c_s$ . Equation (iii) then reduces to:

$$[\text{H}^+] = \frac{c_a}{c_s} \cdot K_a, \quad \text{or} \quad [\text{H}^+] = \frac{[\text{Acid}]}{[\text{Salt}]} \times K_a \quad (\text{iv})$$

$$\text{or } \text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \quad (\text{v})$$

Similarly for a mixture of a weak base of dissociation constant  $K_b$  and its salt with a strong acid:

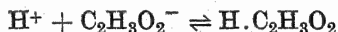
$$[\text{OH}^-] = \frac{[\text{Base}]}{[\text{Salt}]} \times K_b \quad (\text{vi})$$

or

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \quad (\text{vii})$$

A simple example is a mixture of ammonia and ammonium chloride solution: the  $\text{OH}^-$  concentration has a small value, which is sufficient to precipitate the hydroxides of the Group IIIA metals with small solubility products but not those of the metals of the later Groups.

Let us confine our attention to the case in which the concentrations of the acid and its salt are equal, *i.e.* of a half neutralised acid. Then  $\text{pH} = \text{p}K_a$ . Thus the  $\text{pH}$  of a half neutralised solution of a weak acid is equal to the negative logarithm of the dissociation constant of the acid. For acetic acid  $K_a = 1.82 \times 10^{-5}$ ,  $\text{p}K_a = 4.74$ ; a half neutralised solution of, say,  $0.1M$  acetic acid will have a  $\text{pH}$  of 4.74. If one adds a small concentration of  $\text{H}^+$  ions to such a solution, the former will combine with the acetate ions to form undissociated acetic acid.



Similarly, if a small concentration of hydroxyl ions be added, the latter will combine with the hydrogen ions arising from the dissociation of the acetic acid and form unionised water; the equilibrium will be disturbed and more acetic acid will dissociate to replace the hydrogen ions removed in this way. In either case, the concentrations of the acetic acid and acetate ion (or salt) will not be appreciably changed. It follows from equation (v) that the  $\text{pH}$  of the solution will not be materially affected.

The solution containing equal concentrations of acid and salt, or a half neutralised solution of the acid, has the maximum buffer capacity. Other mixtures also possess considerable buffer capacity, but the  $\text{pH}$  will differ slightly from the half neutralised acid. Thus in a quarter neutralised solution of acid,  $[\text{Acid}] = 3[\text{Salt}]$ :

$$\begin{aligned}\text{pH} &= \text{p}K_a + \log 1/3 = \text{p}K_a + \bar{1}.52, \\ &= \text{p}K_a - 0.48\end{aligned}$$

For a three-quarter neutralised acid,  $[\text{Salt}] = 3[\text{Acid}]$ :

$$\begin{aligned}\text{pH} &= \text{p}K_a + \log 3, \\ &= \text{p}K_a + 0.48\end{aligned}$$

In general, it may be stated that the buffering capacity is maintained for mixtures within the range 1 acid : 10 salt and 10 acid : 1 salt. The approximate  $\text{pH}$  range of a weak acid buffer is:

$$\text{pH} = \text{p}K_a \pm 1;$$

the concentration of the acid is usually of the order 0.05–0.2 molar. Similar remarks apply to weak bases.

The preparation of a buffer solution of a definite  $pH$  is a simple process if the acid (or base) of appropriate dissociation constant is found; small variations in  $pH$  are obtained by variations in the ratio of the acid to the salt concentration. One example is given in Table I, 39, 1.

TABLE I, 39, 1.  $pH$  OF ACETIC ACID—SODIUM ACETATE BUFFER MIXTURES

10 ml. mixtures of  $x$  ml. of 0.2M acetic acid and  $y$  ml. of 0.2M sodium acetate

Acetic Acid ( $x$ ml.)	Sodium Acetate ( $y$ ml.)	$pH$
9.0	1.0	3.72
8.0	2.0	4.05
7.0	3.0	4.27
6.0	4.0	4.45
5.0	5.0	4.63
4.0	6.0	4.80
3.0	7.0	4.99
2.0	8.0	5.23
1.0	9.0	5.57

Before leaving the subject of buffer solutions it is necessary to draw attention to a possible erroneous deduction from equation (v), namely that the hydrogen ion concentration of a buffer solution is dependent only upon the ratio of the concentrations of acid and salt and upon  $K_a$ , and not upon the actual concentrations; otherwise expressed, that the  $pH$  of such buffer mixture should not change upon dilution with water. This is approximately although not strictly true. In deducing equation (ii) concentrations have been substituted for activities, a step which is not entirely justifiable except in dilute solution. Theoretically, the expression controlling buffer action is:

$$a_{H^+} = \frac{a_{HA}}{a_{A^-}} \times K_a = \frac{c_a f_a}{c_s f_{A^-}} \times K_a \quad (\text{viii})$$

where  $a$  and  $f$  refer to activities and activity coefficients respectively of the species indicated in the subscript. The activity coefficient  $f_a$  of an undissociated acid is approximately



unity in dilute aqueous solution. Expression (viii) thus becomes:

$$a_{H^+} = \frac{[\text{Acid}]}{[\text{Salt}] \times f_{A^-}} \times K_a \quad (\text{ix})$$

$$\text{or} \quad pH = pK_a + \log [\text{Salt}]/[\text{Acid}] + \log f_{A^-} \quad (\text{x})$$

The activity coefficient of the ion  $f_{A^-}$  generally increases with decreasing ion concentration, so that when a buffer solution is diluted  $f_{A^-}$  increases and consequently  $a_{H^+}$  will decrease (or  $pH$  will increase). For most practical purposes the change is small, but for precise measurements the change must be taken into account.\* Thus it has been calculated that if a buffer solution containing 0.1*N* acetic acid and 0.1*N* sodium acetate is diluted with an equal volume of water, the  $pH$  changes from 4.52 to 4.58. The addition of neutral salts to a buffer mixture results in a change of the ionic strength of the solution: this will affect the activity coefficients of the ions and therefore the  $pH$  of the solution. The results (due to R. P. Bell, 1952) for the  $pH$  at 20° of a formate buffer at various ionic strengths  $I$  clearly illustrate this point. The ratio  $[\text{HCOOH}]/[\text{HCOO}^-]$  was maintained at 2.96 throughout.

[HCOOH]	[HCOO <sup>-</sup> ]	[NaCl]	$I$	$pH$
0.0296	0.0100	—	0.011	2.18
0.1480	0.0500	—	0.050	2.10
0.2960	0.1000	—	0.100	2.03
0.1776	0.0600	0.0400	0.100	2.03
0.0987	0.0300	0.0667	0.100	2.03

Unless  $K_{therm.}$  is known and activity coefficients are taken into account, it is advisable for accurate work to check the  $pH$  of the buffer solution by means of the hydrogen electrode. The following standard buffer solutions have been proposed, the  $pH$  values refer to 25°: 0.1*M*  $\text{KHC}_2\text{O}_4, \text{H}_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O}$ ,  $pH$  1.48; saturated potassium hydrogen tartrate,  $pH$  3.57; 0.05*M* potassium hydrogen phthalate,  $pH$  4.00; 0.1*M*  $\text{CH}_3\text{COOH} + 0.1\text{M}$   $\text{CH}_3\text{COONa}$ ,  $pH$  4.64; 0.005*M*  $\text{Na}_2\text{B}_4\text{O}_7, 10\text{H}_2\text{O}$ ,  $pH$  9.18 (see also Section A, 4).

A number of examples of calculations involving buffer solutions are given below and should be useful to the student. Interionic effects are not taken into account.

\* For a more detailed discussion, see the author's *Text Book of Quantitative Inorganic Analysis: Theory and Practice*, Second Edition, 1951; R. P. Bell, *Acids and Bases*, 1952 (Methuen).

*Example 19.* Calculate the  $pH$  in a solution which is  $0.1M$  in acetic acid and  $0.2M$  in sodium acetate. ( $K_a = 1.82 \times 10^{-5}$ )

To a first approximation, equation (v):

$$\begin{aligned} pH &= pK_a + \log [\text{Salt}] / [\text{Acid}] \\ &= 4.74 + \log 2/1 = 4.74 + 0.30 \\ &= 5.04 \end{aligned}$$

The hydrogen ion concentration in  $0.1M$  acetic acid is  $1.35 \times 10^{-3}$  g. ion per litre (Section I, 14, *Example 3*), i.e. the solution has a  $pH$  of 2.87.

*Example 20.* Given a solution which is  $0.1M$  in acetic acid and  $0.1M$  in sodium acetate, calculate the  $pH$  when (a) 1 ml. of  $10N$  hydrochloric acid and (b) 2 ml. of  $5N$  sodium hydroxide is added to 1 litre of the buffer solution. (The change in volume of the solution may be neglected.)

The  $pH$  of the solution, computed from equation (v), is 4.74.

(a) The hydrochloric acid is completely ionised: it gives a  $[H^+] = 10/1,000 = 0.01$  g. ion per litre. The  $0.01$  mole of hydrogen ions will combine with  $0.01$  mole of acetate ions to yield  $0.01$  mole of practically undissociated acetic acid. Hence  $[C_2H_3O_2^-] = 0.10 - 0.01 = 0.09$ , and  $[H.C_2H_3O_2] = 0.10 + 0.01$ .

$$\begin{aligned} [H^+] &= K_a \times [H.C_2H_3O_2] / [C_2H_3O_2^-] = 1.82 \times 10^{-5} \\ &\quad \times (0.11/0.09) \\ &= 2.22 \times 10^{-5} \end{aligned}$$

i.e.  $pH = 4.66$

Thus the change in  $pH$  upon adding the strong acid is from 4.74 to 4.66 only. If the strong acid were added to 1 litre of water ( $pH = 7.0$ ), the  $pH$  change would be from 7.0 to  $-\log(0.01) = 2.0$ , i.e. by 5 units. (b) The 2 ml. of  $5N$  sodium hydroxide solution in 1 litre of water gives a concentration of  $0.01$  g. mole of  $NaOH$  per litre. The  $0.01$  mole of  $NaOH$  will neutralise  $0.01$  mole of acetic acid to form  $0.01$  mole of acetate ion. Hence  $[C_2H_3O_2^-] = 0.10 + 0.01 = 0.11$  and  $[H.C_2H_3O_2] = 0.10 - 0.01$ .

$$[H^+] = 1.82 \times 10^{-5} \times (0.09/0.11) = 1.49 \times 10^{-5}$$

or  $pH = 4.83$

Thus the change in  $pH$  upon adding strong alkali to the acetate buffer is from 4.74 to 4.83. If the sodium hydroxide solution were added to 1 litre of water,  $[H^+] = K_w / [OH^-] = 10^{-14} / 0.01 = 1.0 \times 10^{-12}$ , or  $pH = 12$ : thus the change in  $pH$  is from 7.0 to 12, i.e. by about 5  $pH$  units.

## I, 40.

## HYDROLYSIS OF SALTS

Salts may be divided into four main groups:

I, those derived from the strong acids and strong bases, e.g. potassium chloride;

II, those derived from weak acids and strong bases, *e.g.* sodium acetate;

III, those derived from strong acids and weak bases, *e.g.* ammonium chloride; and

IV, those derived from weak acids and weak bases, *e.g.* ammonium formate or aluminium acetate.

When any of these is dissolved in water, the solution, as is well known, is not always neutral in reaction. Interaction occurs with the ions of water and the resultant solution may be neutral, acid or alkaline according to the nature of the salt.

With an aqueous solution of a salt of group I, neither the anions have any tendency to combine with hydrogen ions nor the cations with the hydroxyl ions of water. The equilibrium between the hydrogen and hydroxyl ions in water:



is therefore not disturbed and the solution remains neutral.

Consider, however, a salt MA derived from a weak acid HA and a strong base MOH of the conventional or Arrhenius type (group II). The salt is completely dissociated in aqueous solution:



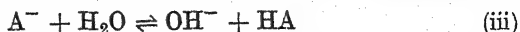
A very small concentration of hydrogen and hydroxyl ions, originating from the small but finite ionisation of water, will be present initially. HA is a weak acid, that is, it is ionised only to a small degree; the concentration of  $\text{A}^-$  ions which can exist in equilibrium with  $\text{H}^+$  ions is accordingly small. In order to maintain the equilibrium the large initial concentration of  $\text{A}^-$  ions must be reduced by combination with  $\text{H}^+$  ions to form unionised HA:



The hydrogen ions required for this reaction can be obtained only from the further dissociation of the water; this dissociation produces simultaneously an equivalent quantity of hydroxyl ions. The hydrogen ions are utilised in the formation of HA, consequently the hydroxyl ion concentration of the solution will increase and the solution will react alkaline. The net result is that the anions of the salt react with the hydrogen ions of water yielding the weak acid HA, and there is an increase in the concentration of hydroxyl ions over that present in water.

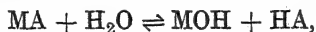
It is usual in writing equations involving equilibria between completely dissociated and slightly dissociated or sparingly

soluble substances to employ the ions of the former and the molecules of the latter. The reaction is therefore written:

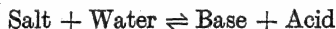


This equation can also be obtained by combining (i) and (ii) since both equilibria must coexist.

This interaction between the ion (or ions) of a salt and the ions of water is called **hydrolysis**. Formerly the chemical reaction was written:



or as:

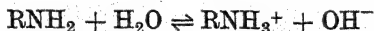


The reaction of the solution was clearly dependent upon the relative strength of MOH and HA. This led to the original, but now obsolete, definition of hydrolysis as the decomposition of a salt by water into an acid and a base.

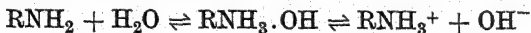
Let us now study the salt of a strong acid and a weak base (group III). The two types of weak bases commonly encountered are metallic hydroxides (such as ferric, aluminium or cupric hydroxides) and ammonia or primary amines  $RNH_2$ . The ultimate ionisation of the former is:



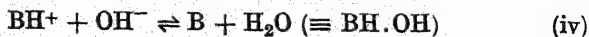
The basic character of ammonia and of amines is best represented as:



The alternative formulation:



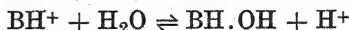
is regarded as less probable, owing to the doubtful existence of  $RNH_3.OH$ ; it leads, however, to the same result. Since those metallic hydroxides which are weak bases are usually poly-acidic and therefore can ionise in stages, it will simplify the discussion if we confine our attention to weak organic bases of the type  $RNH_2$ , where  $R = H$ , alkyl or aryl. We may represent such bases by the symbol B. A salt of such a weak base and a strong acid may be formulated  $(BH)A$ : an example is ammonium chloride  $(NH_3H)Cl$  or  $NH_4Cl$ . In an aqueous solution of a salt  $(BH)A$ , the initial high concentration of cations  $BH^+$  will be reduced by interaction with the hydroxyl ions of water to form the weak base B (or  $BH.OH$ , its hydrated form) until the equilibrium,



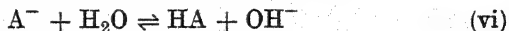
is attained. The hydrogen ion concentration of the solution will thus be increased and the solution will have an acidic reaction. The hydrolysis is here represented by:



or, less probably but possibly more clearly, by:



For salts of group IV in which both the acid and the base are weak, two reactions will occur simultaneously:

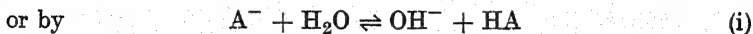
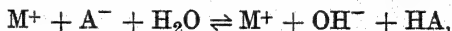


The acidic or basic reaction of the solution will clearly depend upon the relative strengths or dissociation constants of the acid and base. If they are equal in strength, the solution will be neutral; if  $K_a > K_b$ , it will be acidic; and if  $K_b > K_a$ , it will be basic or alkaline.

Having considered the possible cases, we are now in a position to give a more general definition of hydrolysis. **Hydrolysis** is the interaction between the ion (or ions) of a salt and the ions of water with the production of (a) a weak acid or a weak base or (b) of both a weak acid and a weak base.

## I, 41. Hydrolysis Constant and Degree of Hydrolysis.

*Case 1. Salt of a Weak Acid and a Strong Base.* The equilibrium in solution of a salt MA may be represented by:



Applying the law of mass action, one obtains:

$$\frac{a_{\text{OH}^-} \times a_{\text{HA}}}{a_{\text{A}^-}} = \frac{[\text{OH}^-] \cdot [\text{HA}]}{[\text{A}^-]} \times \frac{f_{\text{OH}^-} \cdot f_{\text{HA}}}{f_{\text{A}^-}} = K_h \quad (\text{ii})$$

where  $a$ ,  $f$  and  $[ ]$  refer to activities, activity coefficients and concentrations respectively, and  $K_h$  is the **hydrolysis constant**. The solution is assumed to be dilute; the activity of the unionised water may be then taken as constant. In dilute solutions, the ionic strength is small, and the approximation that the activity coefficient of the unionised acid is unity and also  $f_{\text{OH}^-}/f_{\text{A}^-} = 1$  may be introduced. Equation (ii) then reduces to:

$$K_h = \frac{[\text{OH}^-] \times [\text{HA}]}{[\text{A}^-]} \quad (\text{iii})$$

This is often written in the form:

$$K_h = \frac{[\text{Base}] \times [\text{Acid}]}{[\text{Unhydrolysed Salt}]} \quad (\text{iv})$$

the free strong base and the unhydrolysed salt are completely ionised and the acid is very little dissociated.

The **degree of hydrolysis** is the fraction of each gram molecule hydrolysed at equilibrium. If  $c$  is the concentration of the salt in gram moles per litre and  $x$  is the degree of hydrolysis, then the concentrations of the various species in gram moles or gram ions per litre are:

$$[\text{OH}^-] = xc; [\text{HA}] = xc; \text{ and } [\text{A}^-] = (1 - x)c$$

The substitution of these values in (iii) gives:

$$K_h = \frac{[\text{OH}^-] \times [\text{HA}]}{[\text{A}^-]} = \frac{xc \times xc}{(1 - x)c} = \frac{x^2c}{(1 - x)} \quad (\text{v})$$

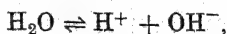
The expression enables one to calculate the degree of hydrolysis  $x$  from the value of the hydrolysis constant  $K_h$  and the concentration  $c$ . It is evident that as the concentration is decreased (*i.e.* the dilution is increased), the degree of hydrolysis  $x$  must increase. The expression (v) is a quadratic equation for  $x$  and the solution is:

$$x = -\frac{K_h}{2c} + \sqrt{\frac{K_h^2}{4c^2} + \frac{K_h}{c}} \quad (\text{vi})$$

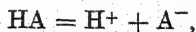
If  $x$  is small ( $< 2\text{--}5$  per cent), (v) reduces to  $K_h = x^2c$

and 
$$x = \sqrt{K_h/c} \quad (\text{vii})$$

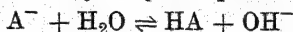
The two equilibria:



and



must coexist with the hydrolytic equilibrium:



Hence the two relationships:

$$[\text{H}^+] \times [\text{OH}^-] = K_w$$

and

$$[\text{H}^+] \times [\text{A}^-] / [\text{HA}] = K_a,$$

must hold in the same solution as:

$$[\text{OH}^-] \times [\text{HA}] / [\text{A}^-] = K_h$$

But 
$$\frac{K_w}{K_a} = \frac{[\text{H}^+] \times [\text{OH}^-] \times [\text{HA}]}{[\text{H}^+] \times [\text{A}^-]} = \frac{[\text{OH}^-] \times [\text{HA}]}{[\text{A}^-]} = K_h,$$

therefore

$$K_w / K_a = K_h \quad (\text{viii})$$

or

$$pK_h = pK_w - pK_a \quad (\text{ix})$$

The hydrolysis constant is thus related to the ionic product of water and the ionisation constant of the acid. Since  $K_a$  varies slightly and  $K_w$  varies considerably with temperature,  $K_h$  and consequently the degree of hydrolysis will be largely influenced by changes of temperature.

The hydrogen ion concentration of a solution of a hydrolysed salt can be readily computed. The amounts of HA and  $\text{OH}^-$  ions formed as a result of hydrolysis are equal, therefore in a solution of the pure salt in water  $[\text{HA}] = [\text{OH}^-]$ .

If the concentration of the salt is  $c$  gram moles per litre, then:

$$\frac{[\text{HA}] \times [\text{OH}^-]}{[\text{A}^-]} = \frac{[\text{OH}^-]^2}{c} = K_h = \frac{K_w}{K_a},$$

and 
$$[\text{OH}^-] = \sqrt{\frac{c \cdot K_w}{K_a}} \quad (\text{x})$$

or 
$$[\text{H}^+] = \sqrt{\frac{K_w \cdot K_a}{c}}, \text{ since } [\text{H}^+] = K_w / [\text{OH}^-] \quad (\text{xi})$$

$$\therefore \text{pH} = \frac{1}{2} \text{p}K_w + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log c^* \quad (\text{xii})$$

It follows, therefore, that the pH of the solution increases with increasing concentration of the salt, although the degree of hydrolysis decreases.

Equation (xii) can be employed for the calculation of the pH of a solution of a salt of a weak acid and strong base. Thus the pH of a 0.05M solution of sodium benzoate is given by:

$$\text{pH} = 7.0 + 2.10 + \frac{1}{2}(-1.30) = 8.45$$

$$(\text{Benzoic acid: } K_a = 6.37 \times 10^{-5}; \text{p}K_a = 4.20)$$

Such a calculation will provide useful information as to the indicator which should be employed in the titration of a weak acid and strong base. An explanation is thus given for the use of phenolphthalein (pH range 8.3 – 10.0) in the titration of benzoic (or acetic) acid with strong bases.

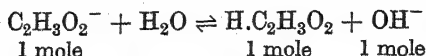
*Example 21.* Calculate (1) the hydrolysis constant, (2) the degree of hydrolysis and (3) the hydrogen ion concentration of a 0.1 molar solution of sodium acetate at the laboratory temperature.

$$K_h = K_w / K_a = 1.0 \times 10^{-14} / 1.82 \times 10^{-5} = 5.5 \times 10^{-10}$$

The degree of hydrolysis  $x$  is given by  $K_h = x^2 c / (1 - x)$ . Substituting for  $K_h$  and  $c$ , and solving the quadratic equation for  $x$ , one obtains  $x = 7.5 \times 10^{-5}$  or 0.0075 per cent.

\* To be consistent one should write  $\text{p}c = -\log c$ .

Alternatively,  $x$  may be deduced by substituting in equations (vi) or (vii)



If the solution were completely hydrolysed, the concentration of acetic acid produced would be  $0.1M$ . But the degree of hydrolysis is  $0.0075$  per cent, therefore the concentration of acetic acid is  $7.5 \times 10^{-6}M$ . This is also equal to the hydroxyl ion concentration produced, i.e.  $p\text{OH} = 5.13$ .

$$p\text{H} = 14.0 - 5.13 = 8.87$$

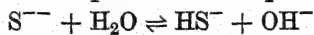
The  $p\text{H}$  may also be computed from equation (xii):

$$\begin{aligned} p\text{H} &= \frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}\log c \\ &= 7.0 + 2.37 + \frac{1}{2}(-1) = 8.87 \end{aligned}$$

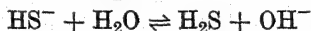
If the degree of hydrolysis is calculated for a  $0.01M$  solution of sodium acetate, it is found to be  $0.0235$  per cent, and the  $p\text{H}$  is  $8.37$ .

*Example 22.* Calculate (1) the degree of hydrolysis and (2) the  $p\text{H}$  of a  $0.1$  molar solution of sodium sulphide at the laboratory temperature. (For  $\text{H}_2\text{S}$ :  $K_1 = 9.1 \times 10^{-8}$ ;  $K_2 = 1.2 \times 10^{-15}$ .)

The hydrolysis of the sulphide ion takes place in two steps:



and



The contribution of the  $\text{OH}^-$  ions from the second step is negligibly small and hence only the primary hydrolysis need be considered. The  $\text{HS}^-$  is effectively the weak acid in this reaction, hence the secondary ionisation constant ( $K_2 = [\text{S}^{--}] \times [\text{H}^+] / [\text{HS}^-]$ ) is employed in the calculation of the hydrolysis constant.

$$K_h = K_w / K_2 = 1.0 \times 10^{-14} / 1.2 \times 10^{-15} = 8.3$$

Let  $x$  be the degree of hydrolysis, then:

$$K_h = 8.3 = \frac{[\text{HS}^-] \times [\text{OH}^-]}{[\text{S}^{--}]} = \frac{x^2c}{(1-x)} = \frac{0.1x^2}{(1-x)}$$

i.e.

$$x^2 + 83x - 83 = 0$$

or

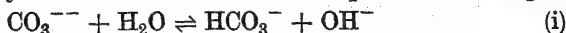
$$x = 0.99 \text{ or } 99 \text{ per cent}$$

The sulphide ion concentration  $= (1-x)c = 0.01 \times 0.1 = 0.001$  mole per litre. Since the solution is almost completely hydrolysed, the hydroxyl ion concentration will be almost  $0.1$  mole and the  $p\text{H}$  accordingly  $13$ .

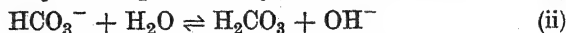
*Example 23.* (a) Calculate (1) the degree of hydrolysis and (2) the  $p\text{H}$  of a  $0.1$  molar solution of sodium carbonate; also (b) calculate the  $p\text{H}$  of a  $0.1$  molar solution of sodium bicarbonate at the laboratory temperature. (For  $\text{H}_2\text{CO}_3$ :  $K_1 = 4.31 \times 10^{-7}$ ;  $K_2 = 5.61 \times 10^{-11}$ .)



(a) The hydrolysis of the carbonate ion takes place in two stages



and



The contribution of the  $\text{OH}^-$  ions from the second step is very small since  $\text{H}_2\text{CO}_3$  is not so weak an acid as  $\text{HCO}_3^-$  and also the  $\text{OH}^-$  ions produced in (i) will tend to diminish the hydrolysis of  $\text{HCO}_3^-$  in (ii), hence only the primary hydrolysis need be considered.

$$K_h = K_w / K_a = 1.0 \times 10^{-14} / 5.61 \times 10^{-11} = 1.79 \times 10^{-4}$$

Let  $x$  = degree of hydrolysis, then:

$$K_h = 1.79 \times 10^{-4} = \frac{[\text{HCO}_3^-] \times [\text{OH}^-]}{[\text{CO}_3^{--}]} = \frac{x^2 \times 0.1}{(1-x)}$$

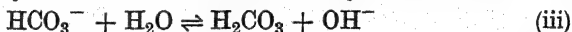
or

$$x = 0.0414 \text{ or } 4.14 \text{ per cent}$$

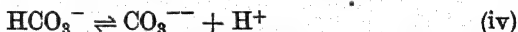
The value of  $x$  deduced from the approximate expression  $x = \sqrt{K_h / c}$  is 0.0423.

$$\begin{aligned} \text{pH} &= \frac{1}{2}\text{p}K_w + \frac{1}{2}\text{p}K_a + \frac{1}{2} \log c \\ &= 7.0 + 5.13 + \frac{1}{2}(-1) = 11.62 \end{aligned}$$

(b) The hydrolysis of the bicarbonate ion may be written:



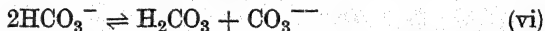
The ionisation of the bicarbonate ion itself must also be taken into account:



this is, in fact, the secondary ionisation of carbonic acid. Since the equilibrium:



coexists with (iii) and (iv), we may write:



Upon combining the equations for the primary and secondary dissociation constants for carbonic acid, we obtain:

$$\begin{aligned} \frac{[\text{H}^+] \times [\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \cdot \frac{[\text{H}^+] \times [\text{CO}_3^{--}]}{[\text{HCO}_3^-]} &= \frac{[\text{H}^+]^2 \times [\text{CO}_3^{--}]}{[\text{H}_2\text{CO}_3]} \\ &= K_1 \times K_2 = 2.42 \times 10^{-17} \quad (\text{vii}) \end{aligned}$$

Now  $[\text{H}_2\text{CO}_3] = [\text{CO}_3^{--}]$  by equation (vi), hence:

$$[\text{H}^+]^2 = K_1 \times K_2 = 2.42 \times 10^{-17}$$

$$[\text{H}^+] = \sqrt{2.42 \times 10^{-17}} = 4.91 \times 10^{-9} \text{ gram ions per litre}$$

or

$$\text{pH} = 8.31$$

The experimental value obtained by glass electrode measurements is  $\text{pH} = 8.18$ , indicating that the calculation is substantially correct.

**Case 2. Salt of a Strong Acid and a Weak Base.** For the sake of simplicity we will consider the salt  $(\text{BH})\text{A}$  derived from

a weak organic base B and a strong acid HA (see Section I, 40). The hydrolytic equilibrium is represented by:



By applying the law of mass action along the lines of *Case 1*, the following equations are obtained:

$$K_h = \frac{[\text{H}_3\text{O}^+] \times [\text{B}]}{[\text{BH}^+]} = \frac{[\text{Acid}] \times [\text{Base}]}{[\text{Unhydrolysed Salt}]} = \frac{K_w}{K_b} \quad (\text{xiv})$$

$$= \frac{x^2c}{(1-x)} \quad (\text{xv})$$

The dissociation constant of the base

$$K_b = [\text{BH}^+] \times [\text{OH}^-] / [\text{B}].$$

Furthermore, since [B] and  $[\text{H}_3\text{O}^+]$  are equal {equation (xiii)},

$$K_h = \frac{[\text{H}_3\text{O}^+] \times [\text{B}]}{[\text{BH}^+]} = \frac{[\text{H}_3\text{O}^+]^2}{(1-x)c} = \frac{[\text{H}_3\text{O}^+]^2}{c} = \frac{K_w}{K_b} \quad (\text{xvi})$$

It is assumed that  $x$  is small ( $<2.5$  per cent).

Hence 
$$[\text{H}_3\text{O}^+] = \sqrt{\frac{K_w \cdot c}{K_b}} \quad (\text{xvii})$$

or 
$$\text{pH} = \frac{1}{2}\text{p}K_w - \frac{1}{2}\text{p}K_b - \frac{1}{2}\log c \quad (\text{xviii})$$

It is evident from equation (xv) that the degree of hydrolysis  $x$  increases with dilution and with decreasing strength of base; also that the pH of the solution must be less than  $\frac{1}{2}\text{p}K_w = 7$ , i.e. the solution has an acidic reaction.

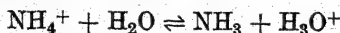
Equation (xviii) can be applied to the calculation of the pH of solutions of salts of strong acids and weak bases. Thus the pH of a 0.2M solution of ammonium chloride is:

$$\text{pH} = 7.0 - 2.37 - \frac{1}{2}(-0.70) = 4.98$$

$$(\text{Ammonia: } K_b = 1.8 \times 10^{-5}; \text{p}K_b = 4.74)$$

*Example 24.* Calculate (1) the degree of hydrolysis and (2) the pH of a 0.1 molar solution of ammonium chloride at the laboratory temperature.

The hydrolysis may be written as:



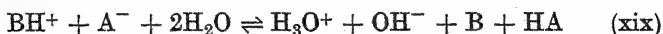
$$K_h = K_w / K_b = 1.0 \times 10^{-14} / 1.8 \times 10^{-5} = 5.6 \times 10^{-10}$$

Now  $K_h = x^2c / (1-x)$ , where  $x$  is the degree of hydrolysis. Substituting for  $K_h$  and  $c$ , and solving the quadratic equation for  $x$ , we find

$$x = 7.5 \times 10^{-5} \text{ or } 0.0075 \text{ per cent}$$

Alternatively  $x$  may be calculated from the relation  $x = \sqrt{K_b / c}$ . The concentration of hydrogen ion  $= xc = 7.5 \times 10^{-5} \times 0.1 = 7.5 \times 10^{-6}$  g. ion per litre, or  $pH = 5.13$ .

**Case 3. Salt of a Weak Acid and a Weak Base.** The hydrolytic equilibrium in a solution of a salt  $(BH)A$ , derived from a weak organic base  $B$  and a weak acid  $HA$ , is expressed by the equation:



Since the normal equilibrium  $2H_2O \rightleftharpoons H_3O^+ + OH^-$  exists in any case, this may be subtracted from (xix); the result may be represented:



The equilibrium constant is given by:

$$K_b = \frac{a_B \times a_{HA}}{a_{BH^+} \times a_{A^-}} = \frac{[B] \cdot [HA]}{[BH^+] \cdot [A^-]} \times \frac{f_B \cdot f_{HA}}{f_{BH^+} \cdot f_{A^-}} \quad (xxi)$$

By making the usual approximations, that is, by assuming that the solution is dilute so that the activity coefficients of the unionised molecules and, less justifiably, of the ions may be taken as unity, the following approximate form of (xxi) is obtained:

$$K_b = \frac{[B] \times [HA]}{[BH^+] \times [A^-]} \quad (xxii)$$

$$= \frac{[Base] \times [Acid]}{[Unhydrolysed Salt]^2} \quad (xxiii)$$

If  $x$  is the degree of hydrolysis in a solution of concentration  $c$  gram mols per litre, the individual concentrations are:

$$[B] = [HA] = xc; [BH^+] = [A^-] = (1 - x)c$$

By substituting these values in (xxii), we obtain:

$$K_b = \frac{xc \times xc}{(1 - x)c \times (1 - x)c} = \frac{x^2}{(1 - x)^2} \quad (xxiv)$$

Furthermore, as in *Case 1*, the expressions:  $K_w = [H^+] \times [OH^-]$ ,  $K_a = [H_3O^+] \times [A^-] / [HA]$ , and  $K_b = [BH^+] \times [OH^-] / [B]$ , hold simultaneously with equation (xxi) for the hydrolytic equilibrium. By substitution in (xxi) it can be readily shown that:

$$K_b = K_w / (K_a \times K_b) \quad (xxv)$$

The solution of equation (xxiv) for the degree of hydrolysis  $x$  is:

$$x = \sqrt{K_b} / (1 + \sqrt{K_b}) \quad (xxvi)$$

If  $K_b$  is small in comparison with unity, then:

$$x = \sqrt{K_b} = \sqrt{K_w / (K_a \times K_b)} \quad (\text{xxvii})$$

This expression, and also (xxv), enable one to calculate  $x$  from the dissociation constants of the acid and the base.

The hydrogen ion concentration of the hydrolysed solution is computed in the following manner:

$$[\text{H}_3\text{O}^+] = K_a \times [\text{HA}] / [\text{A}^-] = K_a \times xc / (1 - x)c = K_a \times x / (1 - x)$$

By equation (xxiv)  $x/(1 - x) = \sqrt{K_b}$ , thus:

$$[\text{H}_3\text{O}^+] = K_a \times \sqrt{K_b} = \sqrt{K_w \times K_a / K_b} \quad (\text{xxviii})$$

or 
$$\text{pH} = \frac{1}{2}\text{p}K_w + \frac{1}{2}\text{p}K_a - \frac{1}{2}\text{p}K_b \quad (\text{xxix})$$

It follows from equations (xxiv) and (xxix) that the degree of hydrolysis and the  $\text{pH}$  are independent of the concentration of the salt; the weaker the acid and the base, the greater will be the extent of hydrolysis. This is strictly true only if  $[\text{BH}^+] = [\text{A}^-]$  and  $[\text{B}] = [\text{HA}]$  as assumed above; this condition will be realised if  $K_a = K_b$  or at least are approximately equal. If the acid  $\text{BH}^+$  and the base  $\text{A}^-$  have different strengths, they will interact with water to different extents (see Section I, 40) and consequently at equilibrium  $[\text{BH}^+]$  and  $[\text{A}^-]$  are not necessarily equal; similar remarks apply to the equilibrium concentrations of B and HA. Fortunately, except in very dilute solution, no significant errors are introduced unless  $K_a$  and  $K_b$  differ by several powers of 10.

If the dissociation constants of the acid and the base are equal, that is,  $K_a = K_b$ ,  $\text{pH} = \frac{1}{2}\text{p}K_w = 7.0$  and the solution is neutral although hydrolysis may be considerable. If  $K_a > K_b$ ,  $\text{pH} < 7$  and the solution is acidic; when  $K_b > K_a$ ,  $\text{pH} > 7$  and the solution reacts basic or alkaline.

The  $\text{pH}$  of a solution of ammonium acetate is given by:

$$\text{pH} = 7.0 + 2.37 - 2.37 = 7.0,$$

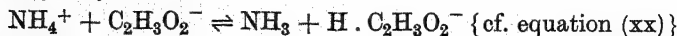
i.e. the solution is approximately neutral. On the other hand, for any solution of ammonium formate:

$$\text{pH} = 7.0 + 1.88 - 2.37 = 6.51,$$

$$(\text{Formic acid: } K_a = 1.77 \times 10^{-4}; \text{p}K_a = 3.75)$$

i.e. the solution reacts slightly acid.

*Example 25.* Calculate the degree of hydrolysis of a 0.1M solution of ammonium acetate at the laboratory temperature. The hydrolytic reaction is:



$$K_b = [\text{NH}_3] \times [\text{H} \cdot \text{C}_2\text{H}_3\text{O}_2] / [\text{NH}_4^+] \times [\text{C}_2\text{H}_3\text{O}_2^-] = K_w / (K_a \times K_b)$$

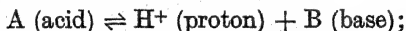
$$= 1.0 \times 10^{-14} / (1.82 \times 10^{-5} \times 1.8 \times 10^{-5}) = 3.1 \times 10^{-5}$$

$K_h$  is clearly small in comparison with unity and we may therefore use equation (xxvii):

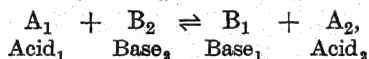
$$x = \sqrt{K_h} = \sqrt{3.1 \times 10^{-5}} = 5.5 \times 10^{-3} \text{ or } 0.55 \text{ per cent}$$

**I, 42. Hydrolysis and the Proton Theory of Acids and Bases.**—If the Brønsted–Lowry definitions of acids and bases (see Section I, 6) are adopted consistently, the term hydrolysis loses much of its original significance. The older and, indeed, firmly established definitions of hydrolysis are merely examples of acid–base reactions when considered in the light of the proton transfer theory of acids and bases.

Before discussing the subject in detail, it is desirable to deal more fully with the subject of acid and conjugate base. The relationship is:

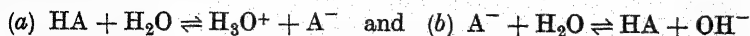


the acid  $A$  and the base  $B$ , which differ by a proton, are said to be **conjugate** to one another. Every acid must, in fact, have its conjugate base and every base its conjugate acid. The interaction of an acid  $A_1$  of one system with a base  $B_2$  of another system may be represented by:



where  $A_1$  and  $B_1$  are the conjugate acid and base of any one system, and  $A_2$  and  $B_2$  are those of the other system. Free protons, because of their great reactivity and small size, do not exist to any extent in solution, and hence the acidic or basic functions of any molecule or ion cannot become manifest unless the solvent molecules can act as proton acceptors or donors respectively, *i.e.* the medium itself must have basic or acidic properties. Solvents are divided roughly into three categories according as the molecules are (1) proton acceptors, *i.e.* basic or **protophilic**; (2) proton donors, *i.e.* acidic or **protogenic**; or (3) neither acceptors nor donors, *i.e.* **aprotic**. A solvent, such as water or an alcohol, which is both protophilic and protogenic is said to be **amphiprotic**. We will confine our attention to water: the conjugate acid and base can function simultaneously and we will study their relative dissociation constants in a given medium.

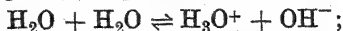
Water can combine with a proton to give the hydroxonium ion  $H_3O^+$ , or it can lose a proton to form the hydroxyl ion  $OH^-$ . The equilibria between the solvent (water) and (a) the acid  $HA$  and (b) its conjugate base  $A^-$  may be written:



The dissociation constants of acid and conjugate base in water are:

$$K_a = a_{\text{H}_3\text{O}^+} \times a_{\text{A}^-} / a_{\text{HA}} \quad \text{and} \quad K_b = a_{\text{HA}} \times a_{\text{OH}^-} / a_{\text{A}^-} \quad (\text{i})$$

The solvent (water) can itself function as an acid and as a base, thus leading to the equilibrium



if the activity of the solvent is assumed to be unity in dilute solution, then:

$$K_w = a_{\text{H}_3\text{O}^+} \times a_{\text{OH}^-} \quad (\text{ii})$$

The quantity  $K_w$  is, of course, the ionic product of water. Upon combining equations (i) and (ii), we obtain the relationship:

$$K_a \times K_b = K_w \quad (\text{iii})$$

that is, the dissociation constant of an acid is inversely proportional to that of its conjugate base, and vice versa, in water (an amphiprotic medium). Otherwise expressed, if the acid is strong, the conjugate base will be weak; if the acid is weak, the conjugate base will be strong.

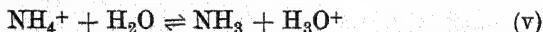
The question of strengths of bases is usually treated separately from acids, but on the proton theory of acids and bases this is really unnecessary, since any protolytic reaction involving an acid must also involve its conjugate base. The older method of evaluating basic strength depended upon the  $\text{OH}^-$  concentration produced in an aqueous solution of a base. Thus the basic dissociation constant of ammonia ( $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$ ) was given by:

$$K_b = [\text{NH}_4^+] \times [\text{OH}^-] / [\text{NH}_3] *$$

The acid dissociation of the ammonium ion may be written as:



this is an abbreviation of:



\* The symbol  $[\text{NH}_3]$  represents the total concentration of undissociated ammonia, irrespective of whether it is present as  $\text{NH}_3$  or as  $\text{NH}_4\text{OH}$ . The two species are related by the equilibrium  $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{OH}$ : since water is present in large excess, the ratio  $[\text{NH}_3] / [\text{NH}_4\text{OH}]$  will be the same in all dilute solutions at the same temperature, hence the form of any equilibrium expression will not be affected by taking into account partial hydration of the undissociated ammonia. If the equilibrium is written  $\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$ , the numerical value for  $K_b$  will be the same order since  $[\text{NH}_4\text{OH}]$  is always taken as equal to the activity (or concentration) of the whole of the ammonia which is not ionised. In actual fact, it is doubtful whether the true  $\text{NH}_4\text{OH}$  exists: it may be a loose hydrogen-bonded complex between ammonia and a water molecule.

The acid dissociation constant of the ammonium ion is:

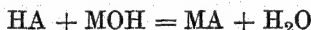
$$K_{\text{B.L.}} = [\text{NH}_3] \times [\text{H}^+] / [\text{NH}_4^+] \quad (\text{vi})$$

Since, to a first approximation,  $K_w = [\text{H}^+] \times [\text{OH}^-]$ , we have:

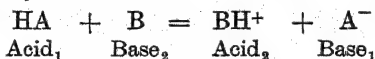
$$K_b = K_w / K_{\text{B.L.}} \quad (\text{vii})$$

This expression enables one to express the "conventional" basic dissociation constant in terms of its conjugate acid.

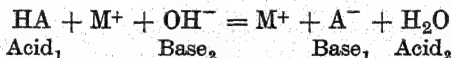
Neutralisation, in the classical sense, may be described as the reaction between equivalent amounts of acid and base (both defined according to Arrhenius) with the production of a salt and water:



If the terms acid and base are employed in the Brönsted-Lowry sense, the product is not necessarily described as a salt and water. The general expression for an acid-base reaction is, as we have already seen in Section I, 6, an example of a proton-transfer or protolytic reaction:

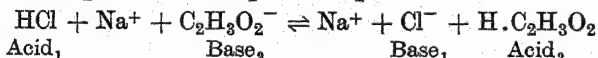


The products of such a reaction are the conjugate acid and the conjugate base of the reactants. If the acid HA and a conventional strong base MOH are neutralised, we may write the reaction:

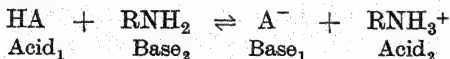


The anion of the acid is thus regarded as a base.

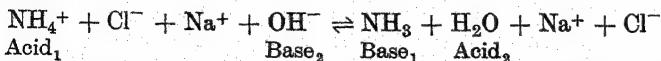
A displacement reaction between the salt of a weak acid and between a strong acid is a neutralisation from the Brönsted-Lowry standpoint. A simple example is:



The neutralisation of ammonia or a primary amine by an acid may be expressed:

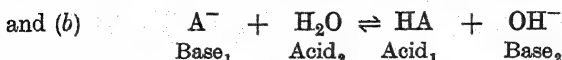
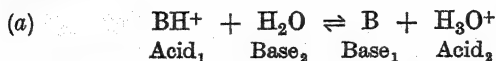


The displacement reaction involving the salt of a weak base and a strong base can also be regarded as a neutralisation, for example:



The extent to which a neutralisation reaction ( $\text{HA} + \text{B} \rightleftharpoons \text{BH}^+ + \text{A}^-$ ) proceeds will depend, not only upon the relative

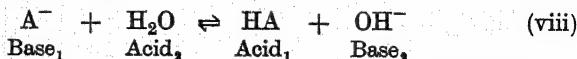
strengths of the two acids concerned, but also upon the nature of the solvent. We are primarily concerned with water, an amphiprotic solvent, which can act as an acid and a base; it may interact with the neutralisation products in two ways:



In (a) the original base is reformed, whereas in (b) the original acid is produced. Hence, in addition to primary neutralisation, further interaction may occur with the solvent which leads to the partial reversal of the neutralisation. The latter is an example of a general phenomenon known as **solvolysis**: when the solvent is water, it is termed **hydrolysis**.

The strength of an acid or a base is, according to equation (vii), inversely proportional to that of its conjugate form. If the acid HA (*e.g.* HCl) is strong, its conjugate base  $\text{A}^-$  (*e.g.*  $\text{Cl}^-$ ) will be very weak and hydrolysis (b) occurs to a negligible extent. If the base used for neutralisation is also strong (*e.g.*  $\text{Na}^+\text{OH}^-$  or, effectively,  $\text{OH}^-$ ), the conjugate acid (*e.g.*  $\text{H}_2\text{O}$ ) will be very weak and consequently reaction (a) will be of little importance. It is clear, therefore, that neutralisation between a strong acid and a strong base in aqueous solution will proceed to completion and no hydrolysis will occur. A necessary corollary is that the salt of a strong acid and a strong base will not be hydrolysed in aqueous solution. When the salt is derived from a weak acid or a weak base or from both a weak acid and a weak base, the corresponding conjugate form or forms will be strong, and appreciable hydrolysis will ensue. The three cases to be considered are those involving (1) a weak acid, (2) a weak base and (3) both a weak acid and a weak base. Each of these will be studied in detail.

Let us first consider the hydrolysis of the salt MA (*e.g.* sodium acetate) of a weak acid HA and a strong base (say,  $\text{M}^+\text{OH}^-$ ) from the Brönsted-Lowry standpoint. The acid HA is weak, consequently the conjugate base  $\text{A}^-$  is reasonably strong. We have the equation (the ions of the metal atom play no part in the reaction):

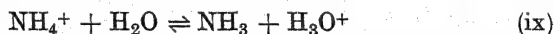


This equation for the hydrolysis reaction is identical with that given in Section I, 41, although the terminology is different.



The expression for the equilibrium constant of this reaction, previously termed the hydrolysis constant, might more suitably be called an acid-base equilibrium constant  $K_{B.L.}$ ; its magnitude is, however, the same irrespective of its name.

The case of the salt  $(BH)A$  of a strong acid  $HA$  and a weak base  $B$  may be treated similarly. To avoid misunderstanding of the general case, let us consider first the specific case of ammonium chloride. This salt may be regarded as derived from the weak base ammonia and the strong acid, hydrochloric acid. The weak base  $NH_3$  will have  $NH_4^+$  as its conjugate acid and the latter will have appreciable strength: this is, in fact, the ion derived from the completely dissociated ammonium chloride. The hydrolytic equilibrium is therefore represented as:



For the general case of the salt  $(BH^+)A^-$ , the equilibrium may be written:



(The anion, *e.g.* chloride or nitrate, has no appreciable acidic or basic properties since it has no detectable tendency to react with the solvent, and therefore will not take part in the equilibrium.) The equilibrium expression for (ix) may be written:

$$K_{B.L.} = \frac{[NH_3] \times [H_3O^+]}{[NH_4^+]} \quad (xi)$$

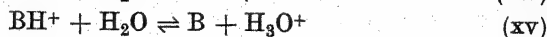
where  $K_{B.L.}$  is the equilibrium constant; it is identical with the acid dissociation constant for the ammonium ion {equation (vi)}. The equilibrium constant for (x) is given by:

$$K_{B.L.} = \frac{[B] \times [H_3O^+]}{[BH^+]} \quad (xii)$$

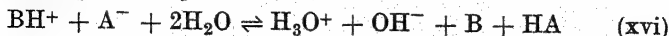
$$= \frac{[Base] \times [Acid]}{[Unhydrolysed Salt]} \quad (xiii)$$

This expression is identical with that deduced on the basis of classical theory in the previous Section.

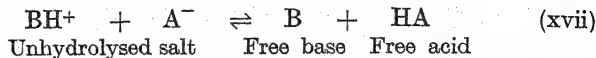
When considering a salt constituted from a weak acid  $HA$  and a weak base  $B$ , it will be realised that the respective conjugate base  $A^-$  and conjugate acid  $BH^+$  have appreciable strength, and so both react with the solvent thus:



By combining both equations, we have:



Since the equilibrium  $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$  exists in any case, we may subtract it from (xvi):

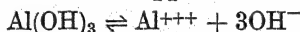


The approximate equilibrium constant is given by:

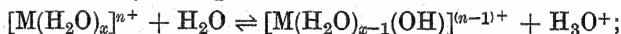
$$K_{\text{B.L.}} = \frac{[\text{B}] \times [\text{HA}]}{[\text{BH}^+] \times [\text{A}^-]} \quad (\text{xviii})$$

This expression for the equilibrium constant, deduced on the basis of the proton theory of acids and bases, is identical with that obtained in Section I, 41 {equation (xxii)}.

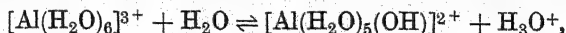
**Metallic Hydroxides as Weak Bases. Hydrolysis of Metallic Ions.**—Many metallic hydroxides, for example those of aluminium, iron, zinc and copper, are weak bases:



There is a considerable volume of evidence that these metallic ions are hydrated (*e.g.*  $[\text{Al}(\text{H}_2\text{O})_6]^{+++}$  and  $[\text{Cu}(\text{H}_2\text{O})_4]^{++}$ ) and these hydrated ions are therefore regarded as the conjugate acids of the corresponding weak bases. The conjugate acids of these weak bases will have appreciable strength {compare equation (iii)}. The primary hydrolysis of the hydrated metallic ions may be represented as:



further hydrolysis may occur under suitable conditions leading ultimately to the precipitation of the metallic hydroxide  $\text{M}(\text{OH})_n$ . Comparatively few quantitative data are at present available for the acid dissociation constants of the hydrated metallic ions {compare acid dissociation constant of the ammonium ion in equation (vi)}. A value of  $1.4 \times 10^{-5}$  has been given for the dissociation constant of the reaction:



and this may serve as a basis for the following illustrative calculation.

*Example 26.* Calculate the *pH* of a 0.1 molar solution of aluminium chloride  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}\text{Cl}_3^{3-}$ .

$$\text{Let } y = [\text{H}_3\text{O}^+] = [\text{Al}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$$

$$K = \frac{[\text{H}_3\text{O}^+] \times [\text{Al}(\text{H}_2\text{O})_5(\text{OH})]^{2+}}{[\text{Al}(\text{H}_2\text{O})_6]^{3+}} = \frac{y^2}{0.1} = 1.4 \times 10^{-5}$$

(compare *Example 3* in Section I, 14).

$$y^2 = 1.4 \times 10^{-6}, y = 1.18 \times 10^{-3} \text{ g. ions per litre,}$$

$$\text{or } \text{pH} = 2.93$$

**I, 43. The Distribution or Partition Law.**—It is a well-known fact that certain substances are more soluble in some solvents than in others. Thus iodine is very much more soluble in carbon disulphide, chloroform or carbon tetrachloride than it is in water. Furthermore, when certain liquids such as carbon disulphide and water, and also ether and water, are shaken together in a vessel and the mixture allowed to stand, the two liquids separate out into two layers. Such liquids are said to be immiscible (carbon disulphide and water) or partially miscible (ether and water), according as to whether they are almost insoluble or partially soluble in one another. If iodine is shaken with a mixture of carbon disulphide and water and then allowed to settle, the iodine will be found to be distributed between the two solvents. A state of equilibrium exists between the solution of iodine in carbon disulphide and the solution of iodine in water. It has been found that when the amount of iodine is varied, the ratio of the concentrations is constant at any given temperature. That is:

$$\frac{\text{Concentration of iodine in carbon disulphide}}{\text{Concentration of iodine in water}} = \frac{C_2}{C_1} = K_d$$

The constant  $K_d$  is known as the **partition** or **distribution coefficient**. Some early (and therefore approximate) experimental results at 18° are collected below.

<i>Grams of iodine in 10 ml. of CS<sub>2</sub> (C<sub>2</sub>)</i>	<i>Grams of iodine in 10 ml. of H<sub>2</sub>O (C<sub>1</sub>)</i>	$K_d = \frac{C_2}{C_1}$
1.76	0.0041	420
1.29	0.0032	400
0.66	0.0016	410
0.41	0.0010	410

It is important to note that the ratio  $C_2/C_1$  is constant only when the dissolved substance has the same molecular weight in both solvents. The **distribution** or **partition law** may be formulated: when a solute distributes itself between two immiscible solvents, there exists for each molecular species, at a given temperature, a constant ratio of distribution between the two solvents, and this distribution ratio is independent of any other molecular species which may be present. The value of the ratio varies with the nature of the two solvents, the nature of the solute, and the temperature.

The distribution law has a number of applications in analysis.

(a) **Removal of bromine and of iodine from aqueous solution.** When an aqueous solution of iodine is shaken with carbon disulphide, the concentration of iodine in the resulting carbon disulphide layer is about 400 times that in water. The carbon disulphide layer may be removed with the aid of a separatory funnel and the process repeated. In this way the concentration of iodine in the aqueous solution may be reduced to a very small value, although theoretically it cannot be removed completely. The distribution coefficients at the laboratory temperature for iodine in  $\text{CHCl}_3/\text{H}_2\text{O}$  and  $\text{CCl}_4/\text{H}_2\text{O}$  are 109 and 85 respectively.

*Example 27.* Ten mg. of iodine are suspended in 12 ml. of water and then shaken with 2 ml. of carbon tetrachloride until equilibrium is reached. Calculate the weight of iodine remaining in the aqueous layer.

Let  $x$  be the weight (mg.) of iodine in the aqueous layer at equilibrium: the concentration will therefore be  $x/12$ . The quantity of iodine (mg.) extracted by the  $\text{CCl}_4$  will be  $(10 - x)$  and its concentration  $(10 - x)/2$ .

$$K_d = 85 = \{(10 - x)/2\} / (x/12)$$

or

$$x = 0.66 \text{ mg.}$$

If the  $\text{CCl}_4$  layer is now withdrawn with the aid of a separatory funnel, and the residual aqueous layer (12 ml.) shaken with a further 2 ml. of  $\text{CCl}_4$  until equilibrium is attained, the quantity  $y$  of iodine remaining in the aqueous layer can be computed from:

$$K_d = 85 = \{(0.66 - y)/2\} / (y/12)$$

$$y = 0.043 \text{ mg.}$$

It can easily be shown that upon withdrawal of the  $\text{CCl}_4$  layer, followed by a further extraction with 2 ml. of the same solvent, the weight of iodine in the aqueous layer is reduced to 0.0028 mg. If instead of three successive extractions with 2 ml. portions of  $\text{CCl}_4$ , the original 10 ml. of the aqueous suspension were treated with 6 ml. of  $\text{CCl}_4$ , the weight of iodine remaining in the aqueous layer would be reduced to 0.23 mg., as can be shown by a calculation similar to the above. This is a simple illustration of the fact that in performing extractions, it is more efficient and also more economical to carry out a number of successive extractions with small portions of the solvent rather than a single extraction with a large quantity.

Use is made of the partition principle in the detection of bromides (Section IV, 15, reaction 5), of iodides (Section IV, 16, reaction 4) and in the detection of bromides and iodides in the presence of each other (Section IV, 44, reaction 8).

(b) **Various tests in qualitative analysis.** (i) "Perchromic acid" (Section IV, 33, reaction 4) is more soluble in amyl alcohol (or in ether) than in water; by shaking the dilute aqueous solution with amyl alcohol (or with ether), a concentrated solution in the latter solvent is obtained, and the presence of chromate or of hydrogen peroxide is indicated by the blue colour.

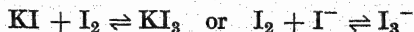
(ii) The compound ammonium cobalthiocyanate,  $(\text{NH}_4)_2[\text{Co}(\text{CNS})_4]$ , produced by the action of a concentrated solution of ammonium thiocyanate upon a cobaltous salt (see Section III, 24, reaction 6), is more soluble in amyl alcohol than in water; the blue coloration of the amyl alcohol layer, due to the formation of a concentrated solution of this compound, is a sensitive and characteristic test for cobalt.

(c) **Study of hydrolysis.** In the hydrolysis of a salt of a weak base and a strong acid or of a weak acid and a strong base, there is an equilibrium between the salt, the free acid and the free base. The hydrolysis, for our present purpose, may be written:



The concentration of the weak acid or of the weak base can be determined by distribution between water and another solvent, such as benzene or chloroform; the partition coefficient of the acid or base between the water and the other solvent must, of course, be known. The degree of hydrolysis may then be calculated from the concentration of the salt and the determined concentration of the weak acid or base. An example of such a salt is aniline hydrochloride. This is partially hydrolysed into aniline and hydrogen chloride. Upon shaking the aqueous solution with benzene, the aniline will distribute itself between the water and benzene in the ratio of the distribution coefficient. The initial concentration of aniline hydrochloride is known, the concentration of the free aniline in the aqueous solution can be computed from that found in the benzene solution, and from this the total concentration of aniline, produced by hydrolysis, is deduced. Sufficient data are then available for the calculation of the degree of hydrolysis.

(d) **The determination of the constitution of complex halide ions.** Iodine is much more soluble in an aqueous solution of potassium iodide than it is in water; this is due to the formation of potassium tri-iodide  $\text{KI}_3$ . The following equilibrium exists in such a solution:

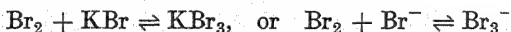


If the solution is titrated with standard sodium thiosulphate solution, the *total* concentration of the iodine, both as free  $I_2$  and combined as  $KI_3$  (or  $I_3^-$ ), is obtained since, as soon as some iodine is removed by interaction with the thiosulphate, a fresh amount of iodine is liberated from the tri-iodide in order to maintain the equilibrium. If, however, the solution is shaken with carbon tetrachloride, in which iodine alone is appreciably soluble, then the iodine in the organic layer is in equilibrium with the *free* iodine in the aqueous solution. By determining the concentration of the iodine in the carbon tetrachloride solution, the concentration of the free iodine in the aqueous solution can be calculated from the known distribution coefficient, and therefrom the total concentration of the free iodine present at equilibrium. Subtracting this from the total iodine, the concentration of the combined iodine (as  $KI_3$ ) is obtained; by subtracting the latter value from the initial concentration of potassium iodide, the concentration of the free KI is deduced. The equilibrium constant:

$$K = \frac{[KI] \times [I_2]}{[KI_3]} \quad \text{or} \quad \frac{[I^-] \times [I_2]}{[I_3^-]}$$

is then computed.

A similar method has been used for the investigation of the equilibrium between bromine and bromides:



Distribution measurements have also been used to prove the existence of the cuprammonium ion  $[Cu(NH_3)_4]^{++}$  in an aqueous ammoniacal solution of copper sulphate, the partition of the free ammonia being studied between chloroform and water:



**I, 44. The Colloidal State.**—It sometimes happens in qualitative analysis that a substance does not appear as a precipitate when the reactants are present in such concentrations that the solubility product of the substance is greatly exceeded and precautions are taken against supersaturation of the resulting solution. Thus when hydrogen sulphide is passed into a cooled solution of arsenious oxide, no precipitate is discernible when one looks through the resulting mixture. The solution, however, has acquired a deep yellow colour and when viewed by reflected light shows a marked opalescence. If a powerful beam of light is passed through the solution and the

latter viewed through a microscope at right angles to the incident light, a scattering of light (bright spots of light against a dark background) is observed, evidently due to the light reflected by the particles in suspension in the solution. The scattering of light is called the **Tyndall effect**, whilst the arrangement of viewing the Tyndall beam in a microscope is termed the **ultramicroscope**. True solutions, *i.e.* those with particles of molecular dimensions do not exhibit a Tyndall effect, and are said to be "optically empty." Clearly the reaction has taken place forming arsenious sulphide but particles are in such a fine state of division that they do not appear as a precipitate. They are in fact in the **colloidal state** or in **colloidal solution**. Other colloidal solutions which may be encountered in qualitative analysis include ferric, chromic and aluminium hydroxides, cupric, manganous and nickel sulphides, silver chloride and silicic acid.

Further examination of the colloidal solution of arsenious sulphide brings to light other peculiar properties. When an attempt is made to filter the solution, the particles are found to pass right through the filter paper. Also, when the colloidal solution is allowed to stand for a long time, no appreciable settling takes place; no precipitation takes place upon shaking with solid arsenious sulphide, thus ruling out the possibility of supersaturation. The addition of, say, aluminium sulphate solution brings about immediate precipitation of arsenious sulphide, although there is no apparent reaction between the  $\text{Al}^{+++}$  or  $\text{SO}_4^{--}$  and any ion in the solution. Potassium chloride solution produces the same effect but considerably more of it must be added. Any electrolyte, in fact, causes precipitation, *i.e.* **coagulation** or **flocculation** of the colloidal material. Heating the solution also favours coagulation. It is evident that the colloidal state must be avoided in qualitative analysis, and a more detailed account of the phenomenon will therefore be given.

The colloidal state of matter is distinguished by a certain range of particle size, as a consequence of which certain characteristic properties become apparent. Before discussing these, mention must be made of the various units which are employed in expressing small quantities. The most important of these are:

$$1 \text{ micron} = 1 \mu = 10^{-3} \text{ mm.} = 10^{-6} \text{ m.}$$

$$1 \text{ milli-micron} = 1 m\mu = 1 \mu\mu = 10^{-6} \text{ mm.}$$

$$1 \text{ Angstrom unit} = 1 \text{ \AA} = 10^{-10} \text{ m.} = 10^{-7} \text{ mm.} = 0.1 m\mu$$

Colloidal properties are, in general, exhibited by substances of particle size ranging between  $0.2\ \mu$  and  $5\ m\mu$ . Ordinary qualitative filter paper will retain particles up to a diameter of  $1-2 \times 10^{-2}\ \text{mm.}$  or  $10-20\ \mu$ , so that colloidal solutions in this respect behave like true solutions (the size of molecules is of the order  $0.1\ m\mu$  or  $10^{-8}\ \text{cm.}$ ). The limit of vision under the microscope is about  $0.2\ \mu$ , whilst that of the ultra-microscope is about  $5-10\ m\mu$ . Colloidal solutions are not true solutions. Close examination shows that they are not homogeneous, but consist of suspensions of solid or liquid particles in a liquid. Such a mixture is known as a **disperse system**; the liquid (usually water in qualitative analysis) is called the **dispersion medium** and the colloid the **disperse phase**.

An important consequence of the smallness of the size of the particles in a colloidal solution is that the ratio of the surface to the volume is extremely large. Phenomena which depend upon the size of the surface, such as **adsorption**, will therefore play an important part.

The effect of particle size upon the area of the surface will be apparent from the following approximate calculations. The total surface area of 1 ml. of material in the form of a cube of 1 cm. side is 6 sq. cm. When it is divided into cubes of  $10^{-6}\ \text{cm.}$  size (which approximates to many colloidal systems), the total area of the same volume of material is  $6 \times 10^6\ \text{sq. cm.}$

Although colloidal particles cannot be separated from those of molecular dimensions by the use of ordinary filter papers—the best quantitative filter papers retain particles larger than about  $1\ \mu$  in diameter—separation can be effected by the use of special devices. The procedure known as **dialysis** utilises the fact that substances in true solution, provided the molecules are not too large, can pass through membranes of parchment or collodion, while colloidal particles are retained. The separation can also be effected by **ultra-filtration**. Filter papers are impregnated with collodion, or with gelatin subsequently hardened by formaldehyde, thereby making the pores small enough to retain particles of colloidal dimensions. The ultimate size of the pores depends upon the particular paper used and upon the concentration of the solution employed to impregnate it. The solution is poured on the filter and the passage of the liquid is accelerated by suction or by pressure. It may be mentioned that other factors (*e.g.* rates of diffusion and adsorption) in addition to pore size determine whether particles of a given size will pass through an ultra-filter or not.

Colloidal systems, in which a liquid is the dispersion medium,



are often termed **sols** to distinguish them from true solutions: the nature of the liquid is indicated by the use of a prefix, e.g. aquasols, alcosols, etc. The solid produced upon coagulation or flocculation of a sol was originally described as a **gel**, but the name is now generally restricted to those cases in which the whole system sets to a semi-solid state without any supernatant liquid initially. Some authors employ the word **gel** to include gelatinous precipitates, such as aluminium and ferric hydroxides, formed from sols, whereas others refer to them as **coagels**. The process of dispersing a flocculated solid or gel (or coagel) to form a colloidal solution is called **peptisation**.

Colloidal solutions may be divided roughly into two main groups, designated as **lyophobic** (Greek: solvent hating) and **lyophilic** (Greek: solvent loving): when water is the dispersion medium, the terms hydrophobic and hydrophilic are employed. The chief properties of each class are summarised in the following Table,\* but it must be emphasised that the distinction is not an absolute one since some, particularly sols of metallic hydroxides, exhibit intermediate properties.

It may be mentioned that negatively-charged colloids include the sols of metals, sulphur, metallic sulphides, silicic acid, stannic acid, silver halides, gums, starch and certain acid dye-stuffs, whilst sols of metallic hydroxides and of certain basic dye-stuffs usually carry a positive charge.

The stability of a colloidal solution is intimately associated with the electrical charge on the particles. Thus in the formation of an arsenious sulphide sol by precipitation with hydrogen sulphide in faintly acid solution, sulphide ions are primarily adsorbed (since every precipitate has a tendency to adsorb its own ions), and in order to maintain the electro-neutrality of the solution, an equivalent quantity of hydrogen ions is secondarily adsorbed. The hydrogen ions or other ions which are secondarily adsorbed have been termed **counter ions**. Thus the so-called electrical double layer is set up between the particles and the solution. If the electrical double layer is destroyed, the sol is no longer stable, and the particles will flocculate since the concentration is in excess of the solubility product. Thus if barium chloride solution is added, barium ions are preferentially adsorbed by the particles; the orientation of the surface is disturbed and the charge disappears. After flocculation, it is found that the dispersion medium is acid

\* For a more detailed account see, for example, H. B. Weiser, *A Text Book of Colloid Chemistry*, Second Edition, 1949 (J. Wiley), or the appropriate sections in S. Glasstone, *Text Book of Physical Chemistry*, Second Edition, 1946.

HYDROPHOBIC SOLS	HYDROPHILIC SOLS
<p>1. The viscosity of the sols is similar to that of the medium. Examples: sols of the metals, silver halides, metallic hydroxides and barium sulphate.</p> <p>2. A comparatively minute quantity of an electrolyte results in flocculation. The change is, in general, irreversible; water has no effect upon the flocculant.</p> <p>3. The particles, ordinarily, have an electric charge of definite sign, which can be changed only by special methods. The particles migrate in one direction in an electric field (<b>cataphoresis</b> or <b>electrophoresis</b>).</p> <p>4. The ultramicroscope reveals bright particles in vigorous motion (<b>Brownian movement</b>).</p> <p>5. The surface tension is similar to that of water.</p>	<p>1. The viscosity is very much higher than that of the medium; they set to jelly-like masses, often termed gels (or coagels). Examples: sols of silicic acid, stannic oxide, gelatin, starches and proteins.</p> <p>2. Small quantities of electrolytes have little effect: large amounts may cause precipitation, "salting out." The change is, in general, reversible upon the addition of water.</p> <p>3. The particles change their charge readily, <i>e.g.</i> they are positively charged in acid medium and negatively charged in a basic medium. Uncharged particles are also known. The particles may migrate in either direction or not at all in an electric field.</p> <p>4. Only a diffuse light is exhibited in the ultramicroscope.</p> <p>5. The surface tension is often lower than that of water: foams are often produced readily.</p>

owing to the liberation of the hydrogen counter ions. It appears that ions of opposite charge to those primarily adsorbed on the surface are necessary for coagulation. The minimum amount of electrolyte necessary to cause flocculation is called the **flocculation** or **coagulation value**. It has been found that the latter depends upon the valency of the ions of the opposite charge to that on the colloidal particle, the higher the valency the smaller the coagulation value; the nature of the ions has some influence also. If two sols of opposite charge are mixed (*e.g.* ferric hydroxide and arsenious sulphide), mutual coagulation usually occurs because of the neutralisation of charges.

The above remarks apply largely to hydrophobic sols.

Hydrophilic sols are generally much more difficult to flocculate than hydrophobic sols. If a small amount of a hydrophilic sol (preferably, but not necessarily, with the same charge), *e.g.* gelatin, is added to a hydrophobic sol, *e.g.* of gold, then the latter appears to be strongly protected against the flocculating action of electrolytes. It may be that the particles of the lyophilic sol are adsorbed by the lyophobic sol and impart their properties to the latter. The hydrophilic substance is known as a **protective colloid**. An explanation is thus provided of the relative stability of the otherwise unstable gold (or other noble metal) sols produced by the addition of a little gelatin or of the salts of protalbic or lysalbic acids (the latter are obtained by the alkaline hydrolysis of albumin). For this reason organic matter, which might form a protective colloid, is generally destroyed before proceeding with an analysis.

During the flocculation of a colloid by an electrolyte, the ion of opposite sign to that of the colloid is adsorbed to a varying degree on the surface; the higher the valency of the ion, the more strongly is it adsorbed. In all cases, the precipitate will be contaminated by surface adsorption. Upon washing the precipitate with water, part of the adsorbed electrolyte is removed, and a new difficulty may arise. The electrolyte concentration in the supernatant liquid may fall below the coagulation value, and the precipitate will pass into colloidal solution again. This phenomenon is known as **peptisation**. It can be prevented by washing the precipitate with a suitable electrolyte.

The adsorptive properties of colloids find some application in analysis, *e.g.* (i) in the removal of phosphates by hydrated stannic oxide in the presence of nitric acid (compare Section VIII, 2), and (ii) in the formation of **coloured lakes** from colloidal metallic hydroxides and certain soluble dyes (see tests for Aluminium in Section III, 21, and for Magnesium in Section III, 33). There is, however, some evidence that lake formation may be partly chemical in character.

Precipitates thrown down from dilute or very concentrated solutions are often in the form of very fine crystals. These fine precipitates will generally become filterable if allowed to stand for some time in contact with the mother liquor, preferably, if the solubility permits, near the boiling point of the solution. The addition of **macerated filter paper**, in the form of a *Whatman filtration accelerator* or as the Schleicher and Schuell (U.S.A.) filter pulp No. 289, is beneficial; the latter is particularly valuable for assisting the filtration of colloidal precipitates. The macerated filter paper increases the speed

of filtration by retaining part of the precipitate and thus preventing the clogging of the pores of the filter paper. When the precipitation has taken place from concentrated solution, the crystals are formed so rapidly that they are imperfect. On standing the crystals tend to perfect themselves: very small particles have a greater solubility than larger particles, hence they dissolve and are deposited upon the larger crystals. Occasionally the precipitate first formed is a metastable modification which is changed on standing into a more stable and less soluble state. The process of ageing of precipitates is spoken of as **digestion**.

When a precipitate separates from a solution, it is not always perfectly pure: it may contain varying amounts of impurities dependent upon the nature of the precipitate and the conditions of precipitation. The contamination of the precipitate by substances which are normally soluble in the mother liquor is termed **coprecipitation** (see also Section I, 16). Two important types of coprecipitation must be distinguished. The first is concerned with adsorption at the surface of the particles exposed to the solution, and the second relates to the occlusion of foreign substances during the process of crystal growth from the primary particles. Surface adsorption is, in general, greatest for gelatinous precipitates and least for those of pronounced macro-crystalline character.

Some precipitates are deposited slowly and the solution is in a state of supersaturation for a considerable time. Thus, when calcium oxalate is precipitated in the presence of a high concentration of magnesium ions, the precipitate is practically pure at first, but if it is allowed to remain in contact with the solution, magnesium oxalate forms slowly and the presence of the calcium oxalate precipitate tends to accelerate the formation of the magnesium oxalate. This precipitation (magnesium oxalate) which occurs on the surface of the first precipitate (calcium oxalate) *after* its formation is termed **post-precipitation**. It is often encountered with sparingly soluble substances which form super-saturated solutions; they usually have an ion in common with the primary precipitate. Another example is the precipitation of copper or mercuric sulphide in 0.3*N* hydrochloric acid solution in the presence of zinc ions; zinc sulphide is slowly post-precipitated.

## CHAPTER II

### EXPERIMENTAL TECHNIQUE OF QUALITATIVE INORGANIC ANALYSIS

BEFORE the student attempts to carry out the analytical reactions of the various cations and anions detailed in Chapters III and IV, he should be familiar with the operations commonly employed in qualitative analysis, that is, with the laboratory technique involved. It is assumed that the student has had some training in elementary practical chemistry, such as that given in the author's manual\*; he should be familiar with such operations as solution, evaporation, crystallisation, distillation, precipitation, filtration, decantation, bending of glass tubes, preparation of ignition tubes, boring of corks and construction of a wash bottle. These will therefore be either very briefly discussed or not described at all in the following pages.

Qualitative analysis may be carried out on various scales. In **macro analysis** the quantity of the substance employed is 0.5–1 gram and the volume of solution taken for the analysis is about 20 ml. In what is usually termed **semimicro analysis**, the quantity used for analysis is reduced by a factor of 0.1–0.05, i.e. to about 0.05 gram and the volume of solution to about 1 ml. For **micro analysis** the factor is of the order of 0.01 or less. There is no sharp line of demarcation between semimicro and micro analysis: the former has been called centigram analysis and the latter milligram analysis, but these terms indicate only very approximately the amounts used in the analysis. It will be noted that only the scale of the operations has been reduced; the concentrations of the ions remain unchanged. Special experimental techniques have been developed for handling the smaller volumes and amounts of precipitate, and these will be described in some detail. For routine analysis by students, the choice lies between macro and semimicro analysis. There are many advantages in adopting the semimicro technique; these include:

(i) Reduced consumption of chemicals and the consequent considerable saving in the laboratory budget.

(ii) The greater speed of the analysis, due to working with smaller quantities of materials and the saving of time in

\* *Elementary Practical Chemistry*, 1936 (Blackie & Son Ltd.).

carrying out the various standard operations of filtration, washing, evaporation, saturation with hydrogen sulphide, etc.

(iii) Increased sharpness of separation, *e.g.* washing of precipitates can be carried out rapidly and efficiently when a centrifuge replaces a filter.

(iv) The amount of hydrogen sulphide used is considerably reduced.

(v) Much space is saved both on the reagent shelves and more especially in the lockers provided immediately below the bench for the housing of the individual student's apparatus; the latter merit may be turned to good use by reducing the size of the bench lockers considerably and thus effectively increasing the accommodation of the laboratory.

(vi) The desirability of securing a training in the manipulation of small amounts of material.

For these, and also other, reasons many laboratories now employ semimicro analysis, particularly for the elementary courses. Both macro and semimicro procedures will be given separately in this book in order that the requirements of all types of students may be met. Nevertheless, when the semimicro technique is adopted, students are recommended to read the Sections dealing with macro technique. It may be said that when the general technique of semimicro analysis has been mastered and appreciated, no serious difficulty should be encountered in adapting a macro procedure to the semimicro scale. Apart from drop reactions, few applications of the micro technique will be described in the text.

Qualitative analysis utilises two kinds of tests, dry reactions and wet reactions. The former are applicable to solid substances and the latter to substances in solution. Most of the dry reactions to be described can be used with only minor modifications for semimicro analysis. Dry tests appear to have lost their popularity in certain quarters; they do, however, often provide useful information in a comparatively short time and a knowledge as to how they are carried out is desirable for all students of qualitative analysis. Different techniques are employed for wet reactions in macro, semimicro and micro analysis.

## TECHNIQUE OF MACRO ANALYSIS

### II, 1.

### DRY REACTIONS

**1. Action of heat.** The substance is placed in a small ignition tube (bulb tube), prepared from soft glass tubing, and heated in a Bunsen flame, gently at first and then more strongly. Small test-tubes,  $2\frac{1}{2}$ –3 inches  $\times$   $\frac{1}{4}$ – $\frac{3}{8}$  inch, which are readily obtainable and are cheap, may also be employed. Sublimation may take place, or the material may melt or may decompose with an attendant change in colour, or a gas may be evolved which can be recognised by certain characteristic properties (see Chapter V, Section VII, 2, Preliminary Dry Tests, Test i).

**2. Blowpipe tests.** A luminous Bunsen flame (air holes completely closed), about 2 inches long, is employed for these

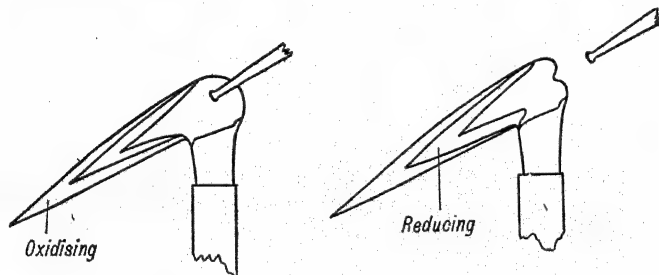


Fig. II, 1, 1

tests. A **reducing flame** is produced by placing the nozzle of a mouth blowpipe just outside the flame, and blowing gently so as to cause the *inner cone* to play on the substance under examination. An **oxidising flame** is obtained by holding the nozzle of the blowpipe about one-third within the flame and blowing somewhat more vigorously in a direction parallel with the burner top; the extreme tip of the flame is allowed to play upon the substance. Fig. II, 1, 1 illustrates the oxidising and reducing flames.

The tests are carried out upon a clean charcoal block in which a small cavity has been made with a pen-knife or with a small coin. A little of the substance is placed in the cavity and heated in the oxidising flame. Decrepitation will occur with crystalline salts; deflagration indicates the presence of

an oxidising agent (nitrate, nitrite, chlorate, etc.). More frequently the powdered substance is mixed with twice its bulk of anhydrous sodium carbonate or, preferably, with "fusion mixture" (an equi-molecular mixture of sodium and potassium carbonates; this has a lower melting point than sodium carbonate alone) in the reducing flame. The initial reaction consists in the formation of the carbonates of the cations present and of the alkali salts of the anions. The alkali salts are largely adsorbed by the porous charcoal, and the carbonates are, for the most part, decomposed into the oxides and carbon dioxide. The oxides of the metals may further decompose, or be reduced, to the metals or they may remain unchanged. The final products of the reaction are therefore either the metals alone, metals and their oxides, or oxides. The oxides of the noble metals (silver and gold) are decomposed without the aid of the charcoal into the metal, which is often obtained as a globule, and oxygen. The oxides of lead, copper, bismuth, antimony, tin, iron, nickel and cobalt are reduced either to a fused metallic globule (Pb, Bi, Sn and Sb) or to a sintered mass (Cu) or to glistening metallic fragments (Fe, Ni and Co). The oxides of cadmium, arsenic and zinc are readily reduced to the metal, but these are so volatile that they vaporise and are carried from the reducing to the oxidising zone of the flame, where they are converted into difficultly volatile oxides. The oxides thus formed are deposited as an incrustation round the cavity of the charcoal block. Zinc yields an incrustation which is yellow while hot and white when cold; that of cadmium is brown and is moderately volatile; that of arsenic is white and is accompanied by a garlic odour due to the volatilisation of the arsenic. A characteristic incrustation accompanies the globules of lead, bismuth and antimony.

The oxides of aluminium, calcium, strontium, barium and magnesium are not reduced by charcoal; they are infusible and glow brightly when strongly heated. If the white residue or white incrustation left on a charcoal block is treated with a drop of cobalt nitrate solution and again heated, a bright blue colour, which probably consists of either a compound or a solid solution of cobaltous and aluminium oxides (Thenard's blue), indicates the presence of aluminium,\* a pale green colour, probably of similar composition (Rinmann's green), is indicative of zinc oxide, and a pale pink mass is formed when magnesium oxide is present (see Chapter VII, Section VII, 2, Preliminary Dry Tests, Test iii).

\* A blue colour is also given by phosphates, arsenates, silicates or borates.



**3. Flame tests.** In order to understand the operations involved in the flame colour tests and the various bead tests to be described subsequently, it is necessary to have some knowledge of the structure of the non-luminous Bunsen flame (Fig. II, 1, 2).

The non-luminous Bunsen flame consists of three parts: (i) an inner blue cone ADB consisting largely of unburnt gas; (ii) a luminous tip at D (this is only visible when the air holes are slightly closed); and (iii) an outer mantle ACBD in which complete combustion of the gas occurs. The principal parts of the flame, according to Bunsen, are clearly indicated in Fig. II, 1, 2. The lowest temperature is at the base of the flame (a);

this is employed for testing volatile substances to determine whether they impart any colour to the flame. The hottest part of the flame is the fusion zone at (b) and lies at about one-third of the height of the flame and approximately equidistant from the outside and inside of the mantle; it is employed for testing the fusibility of substances, and also, in conjunction with (a), in testing the relative volatilities of substances or of a mixture of substances. The lower oxidising zone (c) is situated on the outer border of (b) and may be used for the oxidation of substances dissolved in beads of borax, sodium carbonate or microcosmic salt. The upper oxidising zone (d) consists of the non-luminous tip of the flame; here a large excess of oxygen is present and the flame is not so hot as at (c). It may be used for all oxidation processes in which the highest temperature is not required. The upper reducing zone (e) is at the tip of the inner blue cone and is rich in incandescent carbon; it is especially useful for reducing oxide incrustations to the metal. The lower reducing zone (f) is situated in the inner edge of the mantle next to the blue cone and it is here that the reducing gases mix with the oxygen of the air; it is a less powerful reducing zone than (e), and may be employed for the reduction of fused borax and similar beads.

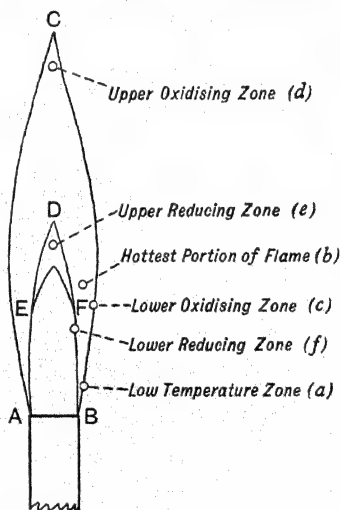


Fig. II, 1, 2

We can now return to the flame tests. Compounds of certain metals are volatilised in the non-luminous Bunsen flame and impart characteristic colours to the flame. The chlorides are amongst the most volatile compounds, and these are prepared *in situ* by mixing the compound with a little concentrated hydrochloric acid before carrying out the tests. The procedure is as follows. A thin platinum wire\* about 5 cm. long and 0.03–0.05 mm. in diameter, fused into the end of a short piece of glass tubing or glass rod which serves as a handle, is employed. This is first thoroughly cleaned by dipping it into concentrated hydrochloric acid contained in a watch glass and then heating it in the fusion zone (b) of the Bunsen flame; the wire is clean when it imparts no colour to the flame. The wire is dipped into concentrated hydrochloric acid on a watch glass, then into a little of the substance whereby a little adheres to the wire. It is then introduced into the lower oxidising zone (c), and the colour imparted to the flame observed. Less volatile substances are heated in the fusion zone (b); in this way it is possible to make use of the difference in volatilities for the separation of the constituents of a mixture.

A table showing the colours imparted to the flame by salts of different metals is given in Chapter V, Section VII, 2, Preliminary Dry Tests, Test (ii). Carry out flame tests with the chlorides of sodium, potassium, calcium, strontium and barium and record the colours you observe. Repeat the test with a mixture of sodium and potassium chlorides. The yellow coloration due to the sodium masks that of the potassium. View the flame through two thicknesses of cobalt glass; the yellow sodium colour is absorbed and the potassium flame appears crimson.

Potassium chloride is much more volatile than the chlorides of the alkaline earth metals. It is therefore possible to detect potassium in the lower oxidising flame and the calcium, strontium and barium in the fusion zone.

After all the tests, the platinum wire should be cleaned with concentrated hydrochloric acid. It is a good plan to store the wire permanently in the acid. A cork is selected that just fits into a test-tube, and a hole bored through the cork through which the glass holder of the platinum wire is passed. The test-tube is about half filled with concentrated hydrochloric

\* If a platinum wire is not available, a short length of chromel (or nichrome) wire, bent into a small loop at one end and inserted into a cork (to serve as a handle) at the other, may be used. This is not as satisfactory as platinum wire and is not recommended.

acid so that when the cork is placed in position, the platinum wire is immersed in the acid.

A platinum wire sometimes acquires a deposit which is removed with difficulty by hydrochloric acid and heat. It is then best to employ fused potassium hydrogen sulphate. A coating of potassium hydrogen sulphate is made to adhere to the wire by drawing the hot wire across a piece of the solid salt. Upon passing the wire slowly through a flame, the bead of potassium pyrosulphate which forms travels along the wire, dissolving the contaminating deposits. When cool, the bead is readily dislodged. Any small residue of pyrosulphate dissolves at once in water, whilst the last traces are usually removed by a single moistening with concentrated hydrochloric acid, followed by heating. The resulting bright clean platinum wire imparts no colour to the flame.

**4. Spectroscopic tests. Flame spectra.** The only trustworthy way to employ flame tests in analysis is to resolve the light into its component tints and to identify the cations present

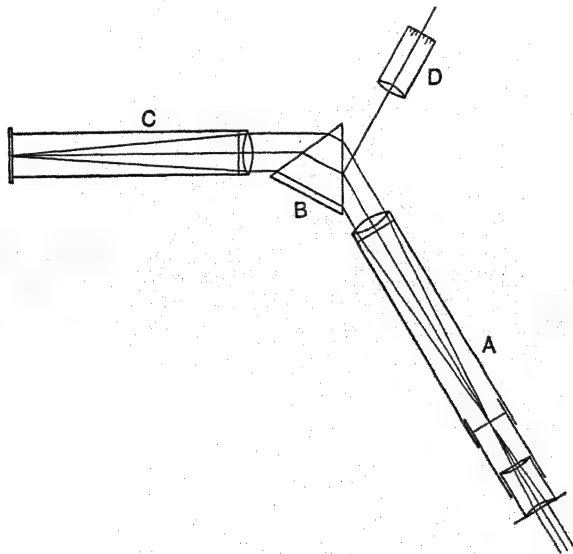


Fig. II, 1, 3

by their characteristic sets of tints. The instrument employed to resolve light into its component colours is called a **spectroscope**. A simple form is shown in Fig. II, 1, 3. It consists of a collimator A which throws a beam of parallel rays on the prism B, mounted on a turn-table; the telescope C through which the spectrum is observed; and a tube D, which contains

a scale of reference lines which may be superposed upon the spectrum. The spectroscope is calibrated by observing the spectra of known substances, such as sodium chloride, potassium chloride, thallium chloride and lithium chloride. The conspicuous lines are located on a graph drawn with wave-lengths as ordinates and scale divisions as abscissae. The wave-length curve may then be employed in obtaining the wave-lengths of all intermediate positions and also in establishing the identity of the component elements of a mixture.

To adjust the simple table spectroscope described above (which is always mounted on a rigid stand), a lighted Bunsen burner is placed in front of the collimator A at a distance of about 10 cm. from the slit. Some sodium chloride is introduced by means of a clean platinum wire into the lower part of the flame, and the tube containing the adjustable slit rotated until the sodium line, as seen through the telescope C, is in a vertical position. (If available, it is more convenient to employ an electric discharge "sodium lamp," such as is marketed by the General Electric Company: this constitutes a high intensity sodium light source.) The sodium line is then sharply focused by suitably adjusting the sliding tubes of the collimator and the telescope. Finally, the scale D is illuminated by placing a small electric lamp in front of it, and the scale sharply focused. The slit should also be made narrow in order that the position of the lines on the scale can be noted accurately.

A smaller, relatively inexpensive and more compact instrument, which is more useful for routine tests in qualitative analysis, is the **direct vision spectroscope** with comparison prism,\* shown in Fig. II, 1, 4.

The light from the "flame" source passes through the central axis of the instrument through the slit, which is adjustable by a milled knob at the side. When the comparison prism is interposed, half the length of the slit is covered and thus light from a source in a position at right angles to the axis of the instrument will fall on one-half of the slit adjacent to the direct light which enters the other half. This light passes through an achromatic objective lens and enters a train of five prisms of the 60° type, three being of crown glass and the alternate two of flint glass. The train of prisms gives an angular dispersion of about 11° between the red and the blue ends of the spectrum. The resulting spectrum, which can

\* The instrument illustrated is the wave-length prism spectroscope (with comparison prism) manufactured by R. and J. Beck Ltd., 69 Mortimer Street, London, W.1. A similar instrument ("hand spectroscope") is manufactured by R. Winkel, G.m.b.H., Königsallee 17-21, Göttingen, Germany: it possesses a number of additional features, which render it very convenient to use for flame and other tests.

be focused by means of a sliding tube adjustment, is observed through the window. There is a subsidiary tube adjacent to the main tube: the former contains a graticule on a glass disc, which is illuminated either from the same source of light as that being observed or from a small subsidiary source (*e.g.* a flash lamp bulb). It is focused by means of a lens system comprising two achromatic combinations between which is a right angle prism. This prism turns the beam of light so that it falls on the face of the end prism (of the train of five prisms) and is reflected into the observer's eye, where it is seen superimposed upon the spectrum. An adjusting screw is provided to alter the position of the right angle prism in

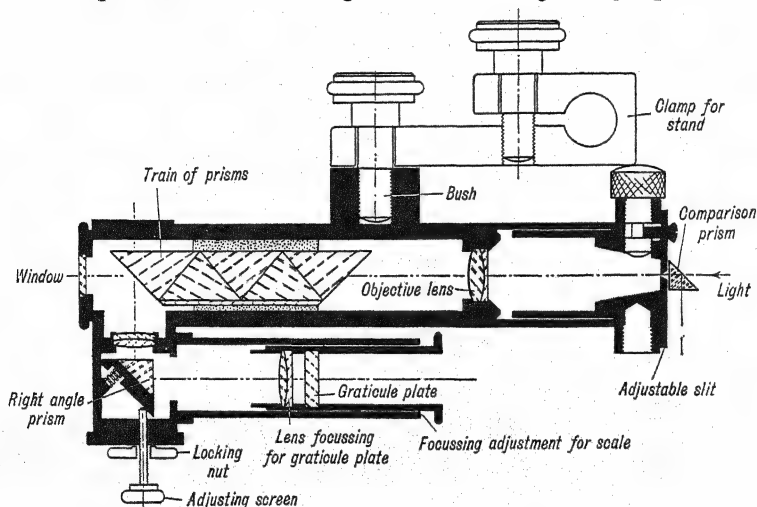


Fig. II, 1, 4

order to adjust the scale relative to the spectrum. The scale is calibrated directly into divisions of 100 angstroms and has also an indication mark at the D-line: it is "calibrated" by means of a sodium source, and the adjusting screw is locked into position by means of a locking nut. The instrument can be mounted on a special stand.

If a sodium compound is introduced into the colourless Bunsen flame, it colours it yellow; if the light is examined by means of a spectroscope, a bright yellow line is visible. By narrowing the slit, two fine yellow lines may be seen. The mean wave-length corresponding to these two lines is  $5893 \times 10^{-7}$  mm. Wave-lengths are generally expressed in Ångstrom units; one Ångstrom unit (or  $1 \text{ Å}$ ) =  $10^{-8}$  cm. =  $10^{-10}$  m.;

sometimes the unit  $\mu\mu$  or  $m\mu$  (milli-micron) is employed to express  $10^{-6}$  mm. or  $10^{-9}$  m. The mean wave-length of the two sodium lines is therefore 5893 Å or 589.3  $m\mu$ . The elements which are usually identified by the spectroscope in qualitative analysis are: sodium, potassium, lithium, thallium and, less frequently, because of the comparative complexity of their spectra, calcium, strontium and barium. The wave-lengths of the brightest lines, visible through a good-quality direct vision spectroscope, are collected in the following table. As already stated, the spectra of the alkaline earth metals are relatively complex and consist of a number of fine lines; the wave-lengths of the brightest of these are given. If the resolution of the spectroscope is small, they will appear as bands.

<i>Element</i>	<i>Description of line(s)</i>	<i>Wave-length in Å</i>
Sodium	Double yellow	5890, 5896
Potassium	Double red	7665, 7699
	Double violet	4044, 4047
Lithium	Red	6708
	Orange (faint)	6103
Thallium	Green	5350
Calcium	Orange band	6182-6203
	Yellowish-green	5554
	Violet (faint)	4227
Strontium	Red band	6744, 6628
	Orange	6060
	Blue	4607
Barium	Green band	5536, 5347, 5243, 5137
	Blue (faint)	4874

The spectra of the various elements are shown diagrammatically in Fig. II, 1, 5; the positions of the lines have been drawn to scale.

A more extended discussion is outside the scope of this volume, and the reader is referred to the standard works on the subject.\*

**5. Borax bead tests.** A platinum wire, similar to that referred to under flame tests, is used for the borax bead tests. The free end of the platinum wire is coiled into a small loop

\* See, for example, W. A. Brode, *Chemical Spectroscopy*, 1943 (J. Wiley; Chapman and Hall); N. H. Nachtrieb, *Principles and Practice of Spectrochemical Analysis*, 1950 (Prentice-Hall).

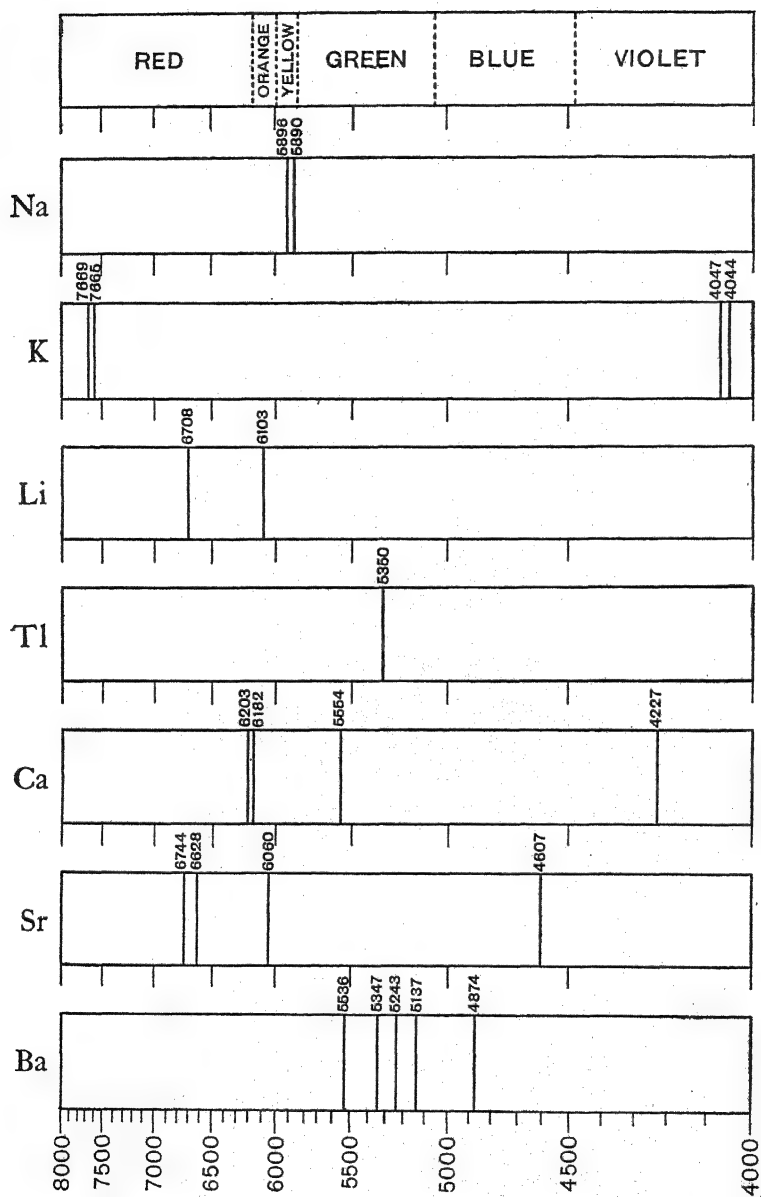


Fig. II, 1, 5

through which an ordinary match will barely pass. The loop is heated in the Bunsen flame until it is red hot and then quickly dipped into powdered borax  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ . The adhering solid is held in the hottest part of the flame; the salt swells up as it loses its water of crystallisation and shrinks upon the loop forming a colourless, transparent, glass-like bead consisting of a mixture of sodium metaborate and boric anhydride:\*

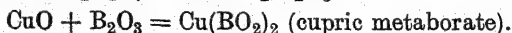
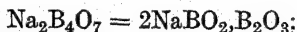


The bead is moistened (this may be done with the tongue) and dipped into the finely powdered substance whereby only a minute amount of the substance will adhere to the bead. It is important to employ a minute amount of substance as otherwise the bead will become dark and opaque in the subsequent heating. The bead and adhering substance is heated first in the lower reducing flame, allowed to cool and the colour observed. It is then heated in the lower oxidising flame, allowed to cool and the colour observed again.

Characteristic coloured beads are produced with salts of copper, iron, chromium, manganese, cobalt and nickel. The student should carry out borax bead tests with salts of these metals and compare his results with those tabulated in Chapter V, Section VII, 2, Preliminary Dry Tests, Test (iv), and also in Chapter IX, Table VI.

After each test, the bead is removed from the wire by heating it again to fusion, and then jerking it off the wire into a vessel of water. The borax bead also provides an excellent method for cleaning a platinum wire; a borax bead is run backwards and forwards along the wire by suitably heating, and is then shaken off by a sudden jerk.

The coloured borax beads are due to the formation of coloured borates; in those cases where different coloured beads are obtained in the oxidising and the reducing flames, borates corresponding to varying stages of oxidation of the metal are produced. Thus with copper salts in the oxidising flame, one has:



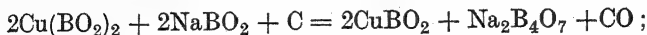
\* Some authors do not recommend the use of a loop on the platinum wire as it is considered that too large a surface of the platinum is thereby exposed. According to their procedure, the alternate dipping into borax and heating is repeated until a bead 1.5–2 mm. in diameter is obtained. The danger of the bead falling off is reduced by holding the wire horizontally. It is the present author's experience that the loop method is far more satisfactory, especially in the hands of beginners, and is less time-consuming.



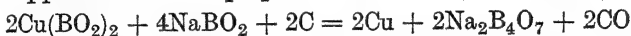
The reaction:



probably also occurs. In the reducing flame (*i.e.* in the presence of carbon), two reactions may take place: (i) the coloured cupric salt is reduced to colourless cuprous metaborate—

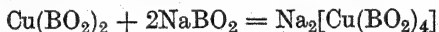


(ii) the cupric borate is reduced to metallic copper, so that the bead appears red and opaque—



With iron salts  $\text{Fe}(\text{BO}_2)_2$  and  $\text{Fe}(\text{BO}_2)_3$  are formed in the reducing and oxidising flames respectively.

Some authors assume that the metal metaborate may combine with sodium metaborate to give complex borates of the type  $\text{Na}_2[\text{Cu}(\text{BO}_2)_4]$ ,  $\text{Na}_2[\text{Ni}(\text{BO}_2)_4]$  and  $\text{Na}_2[\text{Co}(\text{BO}_2)_4]$ :



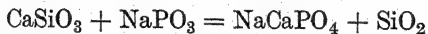
**6. Phosphate or microcosmic salt bead tests.** The bead is produced similarly to the borax bead except that microcosmic salt,  $\text{Na}(\text{NH}_4)\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ , is used. The colourless, transparent bead contains sodium metaphosphate:



This combines with metallic oxides forming orthophosphates, which are often coloured. Thus a blue phosphate bead is obtained with cobalt salts:



The sodium metaphosphate glass exhibits little tendency to combine with acidic oxides. Silica, in particular, is not dissolved by the phosphate bead. When a silicate is strongly heated in the bead, silica is liberated and this remains suspended in the bead in the form of a semi-translucent mass; the so-called silica "skeleton" is seen in the bead during and after fusion. This reaction is employed for the detection of silicates:



It must, however, be pointed out that many silicates dissolve completely in the bead so that the absence of a silica "skeleton" does not conclusively prove that a silicate is not present.

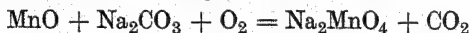
In general, it may be stated that the borax beads are more viscous than the phosphate beads. They accordingly adhere better to the platinum wire loop. The colours of the phosphates, which are generally similar to those of the borax beads,

are usually more pronounced. The various colours of the phosphate beads are collected in the following table.

<i>Oxidising flame</i>	<i>Reducing flame</i>	<i>Metal</i>
Green when hot, blue when cold.	Colourless when hot, red when cold.	Copper
Yellowish- or reddish-brown when hot, yellow when cold.	Yellow when hot, colourless to green when cold.	Iron
Green, hot and cold.	Green, hot and cold.	Chromium
Violet, hot and cold.	Colourless, hot and cold.	Manganese
Blue, hot and cold.	Blue, hot and cold.	Cobalt
Brown, hot and cold.	Grey when cold.	Nickel
Yellow, hot and cold.	Green when cold.	Vanadium
Yellow when hot, yellow-green when cold.	Green, hot and cold.	Uranium
Pale yellow when hot, colourless when cold.	Green when hot, blue* when cold.	Tungsten
Colourless, hot and cold.	Yellow when hot, violet* when cold.	Titanium

\* Blood red when fused with a trace of ferrous sulphate.

**7. Sodium carbonate bead tests.** The sodium carbonate bead is prepared by fusing a small quantity of sodium carbonate on a platinum wire loop in the Bunsen flame; a white, opaque bead is produced. If this is moistened, dipped into a little potassium nitrate and then into a small quantity of a manganese compound, and the whole heated in the oxidising flame, a *green* bead of sodium manganate is formed:



A *yellow* bead is obtained with chromium compounds, due to the production of sodium chromate:



## II, 2.

## WET REACTIONS

These tests are made with substances in solution. A reaction is known to take place (a) by the formation of a precipitate, (b) by the evolution of a gas or (c) by a change of colour. The major number of the reactions of qualitative analysis are carried out in the wet way and details of these are given in later chapters. The following notes upon the methods

to be adopted in carrying out the tests will be found of value and should be carefully studied.

**1. Test-tubes.** The best size for general use is 6 inches  $\times$   $\frac{3}{4}$  inch. It is useful to remember that 10 ml. of liquid fills a test-tube of this size to a depth of about  $1\frac{1}{2}$  inches. Smaller test-tubes are sometimes used for special tests. For heating moderate volumes of liquids a somewhat larger tube, about 7 inches  $\times$  1 inch, the so-called "boiling tube," is recommended. A test-tube brush should be available for cleaning the tubes.

**2. Beakers.** Those of 50, 100 and 250 ml. capacity and of the Griffin form are the most useful in qualitative analysis. Clock glasses of the appropriate size should be provided. For evaporations and chemical reactions which are likely to become vigorous, the clock glass should be supported on the rim of the beaker by means of V-shaped glass rods.

**3. Conical or Erlenmeyer flasks.** These should be of 50, 100 and 250 ml. capacity, and are useful for decompositions and evaporations. The introduction of a funnel, whose stem has been cut off, prevents loss of liquid through the neck of the flask and permits the escape of steam.

**4. Stirring rods.** A length of glass rod, of about 4 mm. diameter, is cut into suitable lengths and the ends rounded in the Bunsen flame. The rods should be about 20 cm. long for use with test-tubes and 8-10 cm. long for work with basins and small beakers. Open glass tubes must not be used as stirring rods. A rod pointed at one end, prepared by heating a glass rod in the flame, drawing it out when soft as in the preparation of a glass jet and then cutting it into two, is employed for piercing the apex of a filter paper to enable one to transfer the contents of a filter paper by means of a stream of water from a wash bottle into another vessel.

A rubber-tipped glass rod or "policeman" is employed for removing any solid from the sides of glass vessels. A stirring rod of polythene (polyethylene) with a thin fan-shaped paddle on each end is available commercially\* and functions as a satisfactory "policeman" at the laboratory temperature: it can be bent into any form.

\* "Police rod" from New York Laboratory Supply Co. Inc., 76 Varick Street, New York, N.Y.13, U.S.A. A similar "police rod" is supplied by Rediweid Ltd., 15/17 Crompton Way, Crawley, Sussex, England.

5. **Wash bottle.** This may consist of a 500 ml. flat-bottomed flask, and the stopper carrying the two tubes should be preferably of rubber (compare Fig. II, 3, 9, a). It is recommended that the wash bottle be kept ready for use filled with hot water as it is usual to wash precipitates with hot water; this runs through the filter paper rapidly and has a greater solvent power than cold water, so that less is required for efficient washing. Asbestos string or cloth should be wound round the neck of the flask in order to protect the hand.

A rubber bulb may be attached to the short tube as in Fig. II, 3, 9, b: this form of wash bottle is highly convenient and is more hygienic than the type requiring blowing by the mouth.

6. **Precipitation.** When excess of a reagent is to be used in the formation of a precipitate, this does not mean that an excessive amount of it should be employed. In most cases, unless specifically stated, only a moderate amount over that required to bring about the reaction is necessary. This is usually best detected by filtering a little of the mixture and testing the filtrate with the reagent; if no further precipitation occurs, a sufficient excess of the reagent has been added. It should always be borne in mind that a large excess of the precipitating agent may lead to the formation of complex ions and consequent partial solution of the precipitate; furthermore, an unnecessary excess of the reagent is wasteful and may lead to complications at a subsequent stage of the analysis.

7. **Precipitation with hydrogen sulphide.** This operation is of such importance in qualitative analysis that it merits a detailed discussion. One method, which is sometimes employed, consists in passing a stream of gas in the form of bubbles through the solution contained in an open beaker, test-tube or conical flask; this procedure is sometimes termed the "bubbling" method. The efficiency of the method is low, particularly in acid solution; absorption of the gas takes place at the surface of the bubbles and, since the gas is absorbed slowly, most of it escapes into the air of the fume chamber and is wasted. It must be remembered that the gas is highly poisonous. *The "bubbling" method is not recommended and should not be used for macro analysis.* The most satisfactory procedure (the "pressure" method) is best described with the aid of Fig. II, 2, 1, a. The solution is contained in a small conical flask A, which is provided with a stopper and lead-in tube: B is a wash bottle containing water and serves to remove any hydrochloric acid spray that might be carried

over from the Kipp's apparatus in the gas stream: C is a stopcock which controls the flow of gas from the generator, whilst stopcock D\* provides an additional control for the gas flow. The conical flask is connected to the wash bottle by a short length of rubber tubing. The stopper is first loosened in the neck of the flask and the gas stream turned on (C first, followed by D) so as to displace most of the air in the flask: this will take not more than about 30 seconds. With the gas flowing, the stopper is inserted tightly and the flask is gently shaken with a rotary motion: splashing of the liquid on to the  $\text{H}_2\text{S}$  delivery tube should be avoided. In order to ensure that all the air has been expelled, it is advisable to loosen the stopper in A again to sweep out the gas and then to tightly

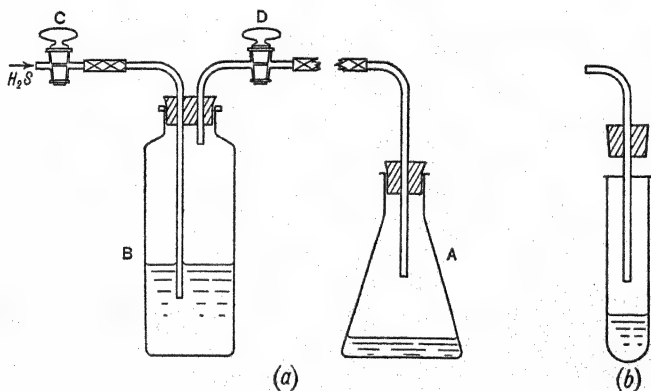


Fig. II, 2, 1

stopper the flask. Passage of the gas is continued with gentle rotation of the flask until the bubbling of the gas in B has almost ceased.† At this point the solution in A should be saturated with hydrogen sulphide and precipitation of the sulphides should be complete: this will normally require only a few minutes. Complete precipitation should be tested for by separating the precipitate by filtration, and repeating the procedure with the filtrate until the hydrogen sulphide produces no further precipitate. Occasionally a test-tube replaces the

\* Stopcock D is optional; it prevents diffusion of air into the wash bottle and thus ensures an almost immediate supply of  $\text{H}_2\text{S}$ .

† It must be borne in mind that the gas may contain a small proportion of hydrogen, due to iron usually present in the commercial ferrous sulphide. Displacement of the gas in the flask (by loosening the stopper) when the bubbling has diminished considerably will ensure complete precipitation.

conical flask; it is shown (with the stopper) in (b). The delivery tube must be thoroughly cleaned after each precipitation. The advantages of the "pressure" method are: (i) a large surface of the liquid is presented to the gas and (ii) it prevents the escape of large amounts of unused gas.

**8. Filtration.** The purpose of filtration is, of course, to separate the mother liquor and excess of reagent from the precipitate. A moderately fine-textured filter paper is generally employed. The size of the filter paper is controlled by the quantity of precipitate and not by the volume of the solution. The upper edge of the filter paper should be about 1 cm. from the upper rim of the glass funnel. It should never be more than about two-thirds full of the solution. Liquids containing precipitates should be heated before filtration except in special cases, such as those containing lead chloride which is more soluble in hot than cold water. Gelatinous precipitates, which usually clog the pores of the filter paper and thus considerably reduce the rate of filtration, may be filtered through fluted filter paper or through a pad of filter papers resting on the plate of a Buchner funnel (Fig. II, 2, 4, B or C): this procedure may be used when the quantity of the precipitate is large and is to be discarded (compare Section III, 20, reaction 8). The best method is to add a little **filter paper pulp** to the solution and then to filter in the normal manner. The filter paper pulp may consist of (a) filter paper clippings, ashless grade, (b) a filtration "accelerator" or "ashless tablet" (Whatman), or (c) "dry-dispersed," ash-free, analytical filter paper pulp (Schleicher and Schuell, U.S.A.). All the various forms of pure filter paper pulp increase the speed of filtration by retaining part of the precipitate and thus preventing the clogging of the pores of the filter paper.

When a precipitate tends to pass through the filter paper, it is often a good plan to add an ammonium salt, such as ammonium chloride or nitrate, to the solution; this will help to prevent the formation of colloidal solutions. The addition of a Whatman filtration "accelerator" may also be advantageous.

A precipitate may be **washed** by decantation, as much as possible being retained in the vessel during the first two or three washings, and the precipitate then transferred to the filter paper. This procedure is unnecessary for coarse, crystalline, easy filterable precipitates as the washing can be carried out directly on the filter paper. This is best done by directing

a stream of water from a wash bottle first around the upper rim of the filter and following this down in a spiral towards the precipitate in the apex; the filter is filled about one-half to two-thirds full at each washing. The completion of washing, *i.e.* the removal of the precipitating agent, is tested for by chemical means; thus if a chloride is to be removed, with silver nitrate solution. If the solution is to be tested for acidity or alkalinity, a drop of the thoroughly stirred solution, removed upon the end of a glass rod, is placed in contact with a small strip of "neutral" litmus paper or of "wide range" or "universal" test paper (Section I, 38) on a watch glass. Other test papers are employed similarly.

**9. Removal of the precipitate from the filter.** If the precipitate is bulky, sufficient for examination can be removed with the aid of a small nickel or stainless steel spatula. If the amount of precipitate is small, one of two methods may be employed. In the first, a small hole is pierced in the base of the filter paper with a pointed glass rod and the precipitate washed into a test-tube or a small beaker with a stream of water from the wash bottle. In the second, the filter paper is removed from the funnel, opened out on a clock glass and scraped with a spatula.

It is frequently necessary to dissolve a precipitate completely. This is most readily done by pouring the solvent, preferably whilst hot, on to the filter and repeating the process, if necessary, until all the precipitate has passed into solution. If it is desired to maintain the volume of the liquid small, the filtrate may be poured repeatedly through the filter until all the precipitate has passed into solution. When only a small quantity of the precipitate is available, the filter paper and precipitate may be heated with the solvent and filtered.

**10. Aids to filtration.** The simplest device is to use a funnel with a long stem, or better to attach a narrow-bored glass tube, about 18 inches long and bent as shown in Fig. II, 2, 2, to the funnel by means of rubber tubing. The lower end of the tube or of the funnel should touch the side of the vessel in which the filtrate is being collected in order to avoid splashing. The speed of filtration depends *inter alia* upon the length of the water column.

Where large quantities of liquids and/or precipitates are to be handled, or if rapid filtration is desired, filtration under diminished pressure is employed: a metal or glass water pump may be used to provide the reduced pressure. A filter flask

of 250–500 ml. capacity is fitted with a two-holed rubber bung: a long glass tube is passed through one hole and a short glass tube, carrying a glass stopcock at its upper end, through the other hole. The side arm of the flask is connected by means of thick-walled rubber tubing ("pressure" tubing) to another



Fig. II, 2, 2

flask, into the mouth of which a glass funnel is fitted by means of a rubber bung. Upon applying suction to the filter paper fitted into the funnel in the usual way, it will be punctured or sucked through, particularly when the volume of the liquid in the funnel is small. To surmount the difficulty, the filter paper must be supported in the funnel. For this purpose either a Whatman filter cone (No. 51) made of a specially hardened filter paper, or a Schleicher and Schuell (U.S.A.) filter paper support (No. 123), made from a muslin-type of material which will not retard filtration, may be used. Both types of support are folded with the filter paper to form the normal type of cone (Fig. II, 2, 3). After the filter paper has been supported in the funnel, filtration may be carried out in the usual manner under the partial vacuum created by the pump, the stopcock T being closed. When filtration is complete, the stopcock T is opened, air thereby entering the apparatus which thus attains atmospheric pressure: the filter funnel may now be removed from the filter flask (Fig. II, 2, 4, a).

For a large quantity of precipitate, a small **Buchner funnel** (b in Fig. II, 2, 4, shown enlarged for the sake of clarity) is

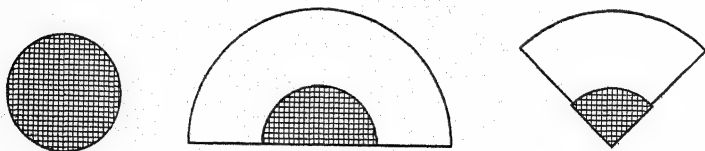


Fig. II, 2, 3

employed. This consists of a porcelain funnel in which a perforated plate is incorporated. Two thicknesses of well-fitting filter paper cover the plate. The Buchner funnel is fitted into the filter flask by means of a cork. When the volume of liquid is small, it may be collected in a test-tube



placed inside the filter flask. The Jena "slit sieve" funnel,\* shown in *c*, is essentially a transparent Buchner funnel; its great advantage over the porcelain Buchner funnel is that it is easy to see whether the funnel is perfectly clean.

Strongly acidic or alkaline solutions cannot be filtered through ordinary filter paper. They may be filtered through a small pad of glass wool or of asbestos placed in the apex of

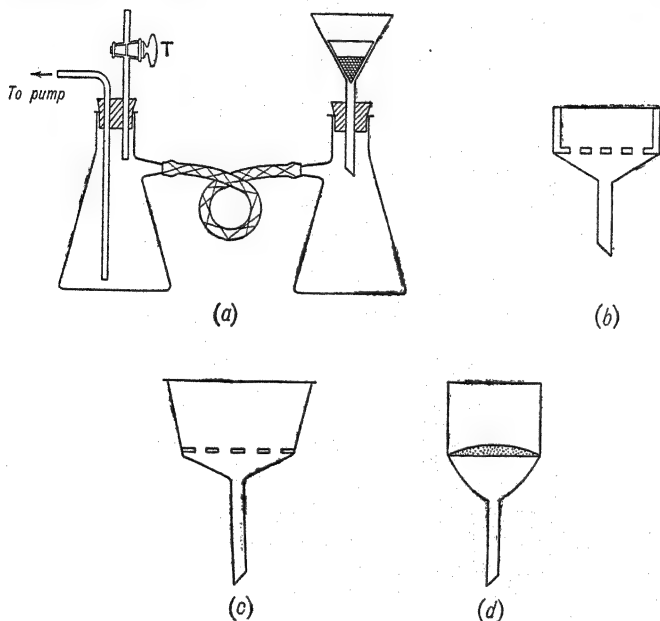


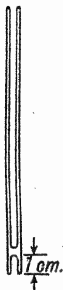
Fig. II, 2, 4

a glass funnel. A more convenient method, applicable to strongly acidic and mildly basic solutions, is to employ a **sintered glass funnel** (Fig. II, 2, 4, *d*): the filter plate, which is available in various porosities, is fused into a resistance glass (borosilicate) funnel. Filtration is carried out under reduced pressure exactly as with a Buchner funnel.

**11. Evaporation.** The analytical procedure may specify evaporation to a smaller volume or evaporation to dryness. Both operations can be conveniently carried out in a porcelain evaporating dish or casserole: the capacity of the vessel should be as small as possible for the amount of liquid being reduced

\* A Pyrex "slit sieve" funnel, with 65 mm. disc, is available commercially.

in volume. The most rapid evaporation is achieved by heating the dish directly on a wire gauze. For many purposes a water bath (a beaker half-filled with water maintained at the boiling point is quite suitable) will serve as a source of heat; the rate of evaporation will of course be slower than by direct heating with a flame. Should corrosive fumes be evolved during the evaporation, the process must be carried out in the fume cupboard. When evaporating to dryness, it is frequently desirable, in order to minimise spattering and bumping, to remove the dish whilst there is still a little liquid left; the heat capacity of the evaporating dish is usually sufficient to complete the operation without further heating.



The reduction in volume of a solution may also be accomplished by direct heating in a small beaker over a wire gauze or by heating in a wide test-tube ("boiling-tube"), held in a holder, by a free flame; in the latter case care must be taken that the liquid does not bump violently. A useful **anti-bumping device**, applicable to solutions from which gases (hydrogen sulphide, sulphur dioxide, etc.) are to be removed by boiling, is shown in Fig. II, 2, 5. It consists of a length of glass tubing sealed off about 1 cm. from one end, and is inserted into the solution. The device must not be used in solutions that contain a precipitate.

**12. Drying of precipitates.** Partial drying, which is sufficient for many purposes, is accomplished by opening out the filter, laying it upon several dry filter papers and allowing them to absorb the water. More complete drying is obtained by placing the funnel containing the filter paper in a "drying cone" (a hollow tinned-iron cone or cylinder), which rests either upon a sand bath or upon a wire gauze and is heated by means of a small flame. The funnel is thus exposed to a current of hot air, which rapidly dries the filter and precipitate. Great care must be taken not to char the filter paper. A safer but slower method is to place the funnel and filter paper, or the filter paper alone resting upon a clock glass, inside a steam oven.

**13. Cleaning of apparatus.** The importance of using clean apparatus cannot be too strongly stressed. All glass-ware should be put away clean. A few minutes should be devoted at the end of the day's work to "cleaning up"; the student should remember that wet dirt is very much easier to

remove than dry dirt. A test-tube brush is provided to clean test-tubes and other glass apparatus. Test-tubes may be inverted in the test-tube stand and allowed to drain. Other apparatus, after rinsing with distilled water, should be wiped dry with a "glass cloth," that is, a cloth which has been washed at least once and contains no dressing.

Glass apparatus which appears to be particularly dirty or greasy is cleaned by soaking in "chromic acid mixture" (concentrated sulphuric acid in which sodium dichromate is dissolved; say, 70 g.  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  per litre), followed by a liberal washing with tap water, and then with distilled water.

**14. Some working hints.** (1) Always work in a tidy, systematic manner. Remember a tidy bench is indicative of a methodical mind. A string duster is useful to wipe up liquids spilt upon the bench. All glass and porcelain apparatus must be scrupulously clean.

(2) Reagent bottles and their stoppers should not be put upon the bench. They should be returned to their correct places upon the shelves immediately after use. If a reagent bottle is empty, it should be returned to the store-room for filling.

(3) When carrying out a test which depends upon the formation of a precipitate, make sure that both the solution to be tested and the reagent is absolutely free from suspended particles. If this is not the case, filter the solutions first.

(4) Do not waste gas or chemicals. The size of the Bunsen flame should be no larger than is absolutely necessary. It should be extinguished when no longer required. Avoid using unnecessary excess of reagents. Reagents should always be added portion-wise.

(5) Pay particular attention to the disposal of waste. Neither strong acids nor strong alkalis should be thrown into the sink; they must be largely diluted first, and the sink flushed with much water. Solids (corks, filter paper, etc.) should be placed in the special boxes provided for them in the laboratory. On no account may they be thrown into the sink.

(6) All operations involving (a) the passage of hydrogen sulphide into a solution, (b) the evaporation of concentrated acids, (c) the evaporation of solutions for the removal of ammonium salts and (d) the evolution of poisonous or disagreeable vapours or gases must be conducted in the fume chamber.

(7) All results, whether positive, negative or inconclusive.

must be recorded neatly in a notebook in ink at the *time they are made*. The writing up of experiments should not be postponed until after the student has left the laboratory. Apart from inaccuracies which may thus creep in, the habit of performing experiments and recording them immediately is one that should be developed from the very outset.

(8) If the analysis is incomplete at the end of the laboratory period, label all solutions and precipitates clearly. It is a good plan to cover these with filter paper to prevent the entrance of dust, etc.

## TECHNIQUE OF SEMIMICRO ANALYSIS

**II, 3. Semimicro apparatus and semimicro analytical operations.**—The essential technique of semimicro analysis does not differ very greatly from that of macro analysis. Since volumes of the order of 1 ml. are dealt with, the scale of the apparatus is reduced; it may be said at once that as soon as the simple technique has been acquired and mastered, the student will find it just as easy to manipulate these small volumes and quantities as to work with larger volumes and quantities in ordinary test-tubes ( $150 \times 20$  mm.) and related apparatus. The various operations occupy less time and the consumption of chemicals and glassware is reduced considerably; these two factors are of great importance when time and money are limited. Particular care must be directed to having both the apparatus and the working bench scrupulously clean.

**1. Test-tubes and centrifuge tubes.** Small Pyrex test-tubes (usually  $75 \times 10$  mm., 4 ml.; sometimes  $100 \times 12$  mm.,

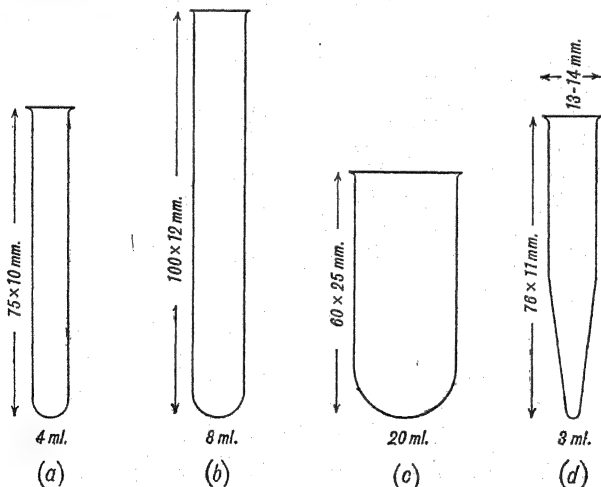


Fig. II, 3, 1

8 ml.) are used for reactions which do not require boiling. When a precipitate is to be separated by centrifuging, a test-tube with a tapered bottom, known as a **centrifuge tube** (Fig. II, 3, 1, d) is generally employed; here, also, the contents

cannot be boiled as "bumping" will occur. Various sizes are available; the 3 ml. centrifuge tube is the most widely used and will be adopted as standard throughout this book. For rapid concentration of a solution by means of a free flame, the **semimicro boiling tube** ( $60 \times 25$  mm., Pyrex; Fig. II, 3, 1, c) will be found convenient.

**2. Stirring rods.** Solutions do not mix readily in semimicro test-tubes and centrifuge tubes: mixing is effected by

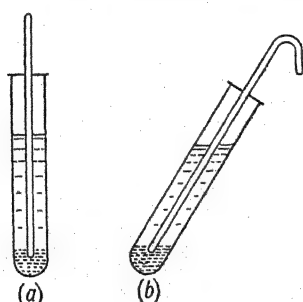


Fig. II, 3, 2

means of stirring rods. These can readily be made by cutting 2 mm. diameter glass rod into 12 cm. lengths. A handle may be formed, if desired, by heating about 1 cm. from the end and bending it back at an angle of  $45^\circ$  (see Fig. II, 3, 2, b). The sharp edges are fire-polished by heating momentarily in a flame. In washing a precipitate with water or other liquid, it is essential to stir the precipitate so that every particle is brought in contact with as large a volume of liquid as possible: this is best done by holding the tube almost horizontal, to spread the precipitate over a large surface, and then stirring the suspension (Fig. II, 3, 2, b).

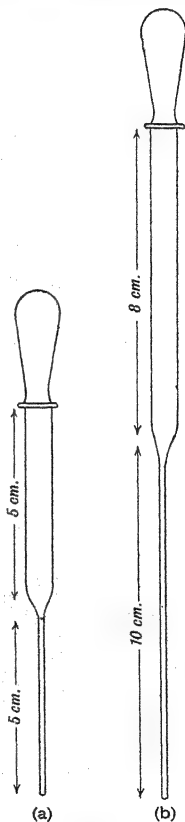


Fig. II, 3, 3

**3. Droppers.** For handling liquids in semimicro analysis, a **dropper** (also termed a dropper pipette) is generally employed. Two varieties are shown in Fig. II, 3, 3, a and b. The former finds application *inter alia* with 30 or 60 ml. (1 or 2 fluid ounce) reagent bottles and may therefore be called a **reagent**

**dropper**; the capillary of the latter (*b*) is long enough to reach to the bottom of a 3 ml. centrifuge tube, and is used for removing supernatant liquids from test-tubes and centrifuge tubes and for the quantitative addition of reagents. Dropper *b* will be named a **capillary dropper**.

Whilst both types of dropper may be purchased, it is quite a simple operation (and excellent practice) to make them from glass tubing. To make a capillary dropper, take a piece of glass tubing about 20 cm. long and of 7 mm. bore and heat it near the middle in a Bunsen or blowpipe flame, rotating slowly all the time. When the centre is soft, allow the glass to thicken *slightly* by continuing the heating and rotating whilst exerting a gentle inward pressure from the ends. Remove the tube from the flame and *slowly* draw out the softened portion to form a fairly thick-walled capillary about 20 cm. long and 2 mm. diameter. When cold, cut the capillary at the mid-point with a file. Fire-polish the capillary ends by rotating in a flame for a moment or two. In order that a rubber bulb (teat) may fit securely on the wide end, heat it cautiously in a flame until just soft, and whilst rotating slowly open it up with a file or glass-worker's triangular "reamer"; alternatively, the softened end of the tube may be quickly pressed down on an asbestos or uralite sheet or upon some other inert surface. A reagent dropper is made in a similar manner except that it is unnecessary to appreciably thicken the middle of the tube before drawing out.

Before use the droppers must be calibrated, *i.e.* the volume of the drop delivered must be known. Introduce some distilled water into the clean dropper by dipping the capillary end into some distilled water in a beaker and compressing and then releasing the rubber teat or bulb. Hold the dropper *vertically* over a clean dry 5 ml. measuring cylinder, and gently press the rubber bulb. Count the number of drops until the meniscus reaches the 2 ml. mark. Repeat the calibration until two results are obtained which do not differ by more than 2 drops. Calculate the volume of a single drop. The dropper should deliver between 30 and 40 drops per ml. Attach a small label to the upper part of the dropper giving the number of drops per ml.

The standard commercial form of **medicine dropper**, with a tip of 1.5 mm. inside diameter and 3 mm. outside diameter, delivers drops of dilute aqueous solutions about 0.05 ml. in volume, *i.e.* about 20 drops per ml. This dropper is somewhat more robust than that shown in Fig. II, 3, 3, *a* as it has a shorter and thicker capillary: this may be an advantage for elementary students, but the size of the drop (*ca.* 20 per ml.) may be slightly too large when working with volumes of the order of 1 ml. However, if this dropper is used, it should be calibrated as described in the previous paragraph.

It must be remembered that the volume of the drop delivered by a dropper pipette depends upon the density, surface tension, etc., of the liquid. If the dropper delivers 20 drops of distilled water, the number of drops per ml. of other liquids will be very approximately as follows: dilute aqueous solutions, 20–22; concentrated hydrochloric acid, 23–24; concentrated nitric acid, 36–37; concentrated sulphuric acid, 36–37; acetic acid, 63; and concentrated ammonia solution, 24–25.

**4. Reagent bottles and reagents.** A semimicro reagent bottle may be easily constructed by inserting a reagent dropper through a cork or rubber stopper that fits a 30 or 60 ml. (1 or 2 fluid ounce) bottle—as in Fig. II, 3, 4, *a*. One or two ounce dropping bottles (Fig. II, 3, 4, *b*) may be purchased\* and are

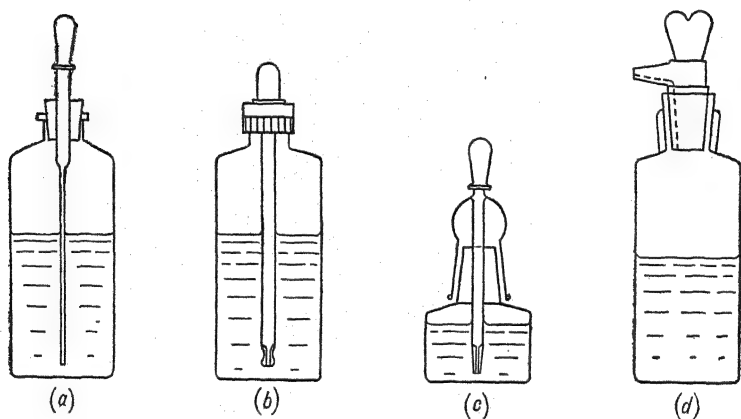


Fig. II, 3, 4

inexpensive: the stoppers of these bottles are usually made of a hard rubber or plastic composition, and this as well as the rubber teat (or bulb) are attacked by concentrated inorganic acids. A dropping bottle of one ounce capacity with an interchangeable glass cap (Fig. II, 3, 4, *c*) is also marketed.† The bottles *a* and *b* cannot be used for concentrated acids and other corrosive liquids because of their action upon the stoppers. The simplest containers for these corrosive liquids are 30 or 60 ml. T.K. dropping bottles (Fig. II, 3, 4, *d*).

Each student should be provided with a solid wooden stand

\* The manufacturers of one satisfactory grade of dropping bottle are Beaton, Clark & Co. Ltd., Rotherham, Yorks; the commercial name is "Bakelite-capped, amber, round eye drops with bulb end pipettes." This firm also supplies the "Stoppered white T.K. dropping bottles."

† Quickfit and Quartz Ltd., "Quickfit" Works, Stone, Staffs.



housing a set of reagents in 30 ml. or, preferably, 60 ml. bottles. The following are used in the author's laboratory.

*Reagent Bottles Fitted with Reagent Droppers*

(Fig. II, 3, 4, a or b)

Sodium hydroxide	5N	Acetic acid, dil.	5N
Ammonium sulphide	6N	Ammonia solution, conc.	15N
Potassium hydroxide	2N	Ammonia solution, dil.	5N
Barium chloride	0.5N	Potassium ferrocyanide	0.5N
Silver nitrate	0.1N	Potassium chromate	0.5N
Ferric chloride	0.5N	Ammonium carbonate	4N

*T.K. Dropper Bottles*

Hydrochloric acid, conc.	12N	Hydrochloric acid, dil.	5N
Sulphuric acid, conc.	36N	Sulphuric acid, dil.	5N
Nitric acid, conc.	16N	Nitric acid, dil.	5N

Some may prefer to have the Ammonia solution, conc. in a T.K. bottle, and the dilute mineral acids in the reagent bottles fitted with reagent droppers. Others may like to have the Hydrochloric acid, dil. of 2.5–3N strength. These are questions of personal preference, and the decision will rest with the teacher.

The other reagents, which are used less frequently, are kept in 60 or 125 ml. dropping bottles (30 ml. for expensive or unstable reagents) on the reagent shelf (**side shelf** or **side rack reagents**); further details of these will be found in the Appendix (Section A, 2). Two sets of these bottles should be available in each laboratory. When using these side shelf reagents, great care should be taken that the droppers do not come into contact with the test solutions, thus contaminating the reagents. If accidental contact should be made, the droppers must be thoroughly rinsed with distilled water and then dried. Under no circumstances should the capillary end of the dropper be dipped into any foreign solution.

**5. The centrifuge.** The separation of a precipitate from a supernatant liquid is carried out with the aid of a centrifuge. This is an apparatus for the separation of two substances of different density by the application of centrifugal force: the latter may be several times that of gravity. In practice, the liquid containing the suspended precipitate is placed in a semi-micro centrifuge tube. The tube and its contents, and a similar tube containing an equal weight of water are placed in diagonally opposite buckets of the centrifuge, and the cover is

placed in position; upon rotation for a short time, allowing the buckets to come to rest and removing the cover, it will be found that the precipitate has separated at the bottom of the tube. This operation (**centrifugation**) replaces filtration in macro analysis. The supernatant liquid can be readily removed by means of a capillary dropper; the clear liquid may be called the centrifugate or "centrate."

The advantages of centrifugation are: (i) speed, (ii) the precipitate is concentrated into a small volume so that small precipitates are observed readily and their relative magnitudes estimated, (iii) the washing of the precipitate can be carried out rapidly and efficiently, and (iv) concentrated acids, bases and other corrosive liquids can be manipulated easily.

The **theory** of the centrifuge is given below. The rate of settling  $r_s$  (cm./sec.) of spherical particles of density  $d_p$  and of radius  $a$  (cm.) in a medium of viscosity  $\eta$  (c.g.s. units) and of density  $d_m$  is given by Stokes' law:

$$r_s = \frac{2a^2g(d_p - d_m)}{9\eta} \quad (1)$$

where  $g$  is the acceleration due to gravity (981 cm./sec.<sup>2</sup>). It is evident from the equation that the rate of settling is increased by: (a) an

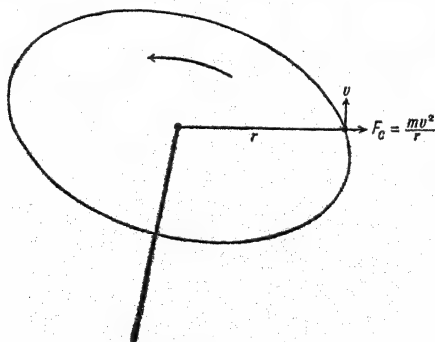


Fig. II, 3, 5

increase in the size of the particles  $a$ ; (b) an increase in difference between the density of the particles  $d_p$  and that of the medium  $d_m$ ; (c) a decrease in the viscosity  $\eta$  of the medium; and (d) an increase in the acceleration due to gravity  $g$ . Fine crystalline particles tend to increase in size when allowed to stand in the liquid in which they are precipitated, particularly when the solution is maintained at elevated temperatures and shaken occasionally. The coagulation of colloidal and gelatinous precipitates is also accelerated by high temperatures and stirring, and also by the addition of certain electrolytes. Moreover, an increase in temperature reduces the viscosity and also increases the difference  $(d_p - d_m)$ . This explains why centrifuge tubes or test-tubes

in which precipitates are formed are usually placed in a hot water bath and shaken from time to time before separation of the mother liquor. The effect of these factors is, however, comparatively small. To accelerate greatly the rate of settling, the force on the particle  $g$  (acceleration due to gravity) must be changed. This is readily and conveniently achieved with the aid of a centrifuge.

The relative rates of settling in a centrifuge tube and in a stationary test-tube may be derived as follows. The centrifugal force  $F_c$  upon a particle of effective mass  $m$  (grams) moving in a circle of diameter  $r$  (cm.) at  $n$  revolutions per second is given by:

$$F_c = ma = \frac{mv^2}{r} = \frac{m(2\pi rn)^2}{r} = m \cdot 4\pi^2 rn^2,$$

where  $a$  is the acceleration (cm./sec.<sup>2</sup>),  $v$  is the velocity (cm./sec.), and  $\pi = 3.1416$ . The gravitational force  $F_g$  on a particle of mass  $m$  is given by:

$$\begin{aligned} F_g &= m \cdot g \\ \frac{F_c}{F_g} &= \frac{m \cdot 4\pi^2 rn^2}{mg} = \frac{4\pi^2 rn^2}{g} \end{aligned}$$

Expressing rotations per second  $n$  in rotations per minute  $N$ , and substituting for  $\pi$ , we have:

$$\frac{F_c}{F_g} = \frac{4\pi^2 r N^2}{981 \times 60^2} = 1.118 \times 10^{-5} r N^2 \quad (2)$$

Thus a centrifuge with a radius of 10 cm. and a speed of 2000 revolutions per minute has a comparative centrifugal force of  $1.118 \times 10^{-5} \times 10 \times (2000)^2 = 447$ , say, 450 times the force of gravity. A precipitate which settles in, say, 10 minutes by the force of gravity alone will settle in  $10 \times 60/450$  or in 1.3 seconds in such a centrifuge. The great advantage of a centrifuge is thus manifest.

Several types of centrifuge are available for semimicro analysis. These are:

A. A small 2-tube hand centrifuge with protecting bowl and cover\* (Fig. II, 3, 6 and Fig. II, 3, 23); if properly constructed it will give speeds up to 2–3000 r.p.m. with 3 ml. centrifuge tubes. The central spindle should be provided with a locking screw or nut: this is an additional safeguard against the possibility of the head carrying the buckets flying off—an extremely rare occurrence. The hand-driven centrifuge is inexpensive and is satisfactory for elementary courses.

B. An inexpensive constant speed, electrically-driven centrifuge (see Figs. II, 3, 22 and II, 3, 23) is marketed† and has a working speed of 1450 r.p.m. It is supplied with a dual-purpose head. The buckets can either “swing out” to the

\* An excellent model is manufactured by Moseley Centrifuge and Engineering Co. of 119 Copenhagen Street, London, N.1.

† “Micro” centrifuge from Measuring and Scientific Equipment Ltd., Spenser Street, London, S.W.1, or from International Equipment Company, 1284 Soldiers Field Road, Boston 35, Mass., U.S.A.

horizontal position or, by means of a rubber adapter, the buckets can be held at a fixed angle of  $45^\circ$  (M.S.E.) or  $51^\circ$  (International); in the latter case, the instrument acts as an "angle" centrifuge. This is an alternative to the hand centrifuge.

C. A variable speed, electrically-driven centrifuge (see Fig. II, 3, 23) with speed indicator\* is the ideal instrument for centrifugation, but is relatively expensive. It is recommended

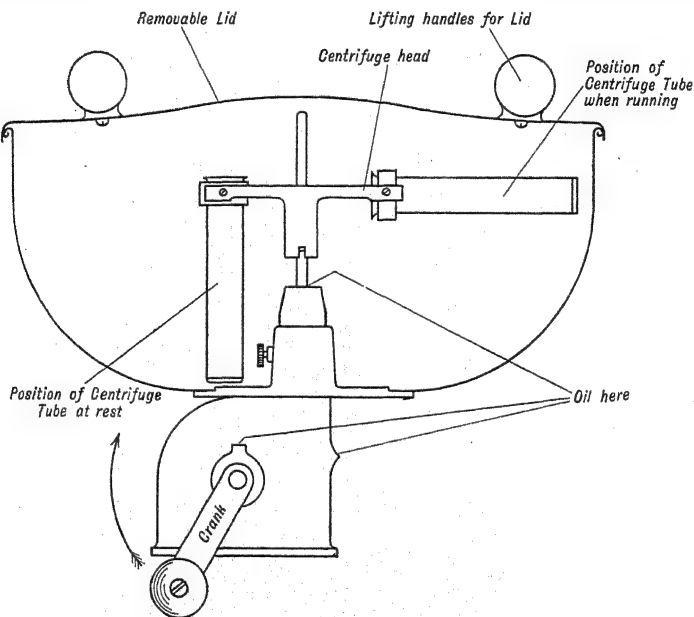


Fig. II, 3, 6

that at least one of these should be available in every laboratory for demonstration purposes.

When using a hand-driven centrifuge, the following points should be borne in mind:

(1) The two tubes should have approximately the same size and weight.

(2) The tube should not be filled beyond 1 cm. from the top. Spilling may corrode the buckets and produce an unbalanced head.

\* "Minor" centrifuge from Measuring and Scientific Equipment Ltd., London: "Clinical model" centrifuge from International Equipment Company, Boston. Controlled speeds to a maximum of about 4000 r.p.m.

(3) Before centrifuging a precipitate contained in a centrifuge tube, prepare a balancing tube by adding sufficient distilled water from a dropper to an empty tube of the same capacity until the liquid levels in both tubes are approximately the same.

(4) Insert the tubes in diametrically opposite positions in the centrifuge; the head (sometimes known as a rotor) will then be balanced and vibration will be reduced to a minimum. Fix the cover in place.

(5) Start the centrifuge slowly and smoothly, and bring it to the maximum speed with a few turns of the handle. Maintain the maximum speed for 30–45 seconds, and then allow the centrifuge to come to rest of its own accord by releasing the handle. Do not attempt to retard the speed of the centrifuge with the hand. A little practice will enable one to judge the exact time required to pack the precipitate tightly at the bottom of the tube. It is of the utmost importance to avoid strains or vibrations as these may result in stirring up the mixture and may damage the apparatus.

(6) Before commencing a centrifugation, see whether any particles are floating on the surface of the liquid or adhering to the side of the tube. Surface tension effects prevent surface particles from settling readily. Agitate the surface with a stirring rod if necessary, and wash down the side of the centrifuge tube using a capillary dropper and a small volume of water or appropriate solution.

(7) Never use centrifuge tubes with broken or cracked lips.

The instructions for use of constant speed, electrically-driven centrifuges are similar to those given above with the addition of the following:

(8) Never leave the centrifuge while it is in motion. If a suspicious sound is heard, or you observe that the instrument is vibrating or becomes unduly hot, turn off the current at once and report the matter to the teacher. An unusual sound may be due to the breaking of a tube; vibration suggests an unbalanced condition.

(9) If a variable speed, electrically-driven centrifuge is employed, switch the current on with the resistance fully in circuit: gradually move the resistance over until the necessary speed is attained. (For most work, it is neither necessary nor desirable to utilise the full speed of the centrifuge.) After 30–45 seconds, move the slider (rheostat arm) back to the original position: make certain that the current is switched off. Allow 30 seconds for the centrifuge to come to rest, then raise the lid and remove the tubes.

Most semimicro centrifuges will accommodate both semimicro test-tubes ( $75 \times 10$  mm.) and centrifuge tubes (up to 5 ml. capacity). The advantages of the latter include (a) easier removal of the mother liquor with a dropper, and (b) with small quantities of solids, the precipitate is more clearly visible (and the relative quantity is therefore more easily estimated) in a centrifuge tube (Fig. II, 3, 7).

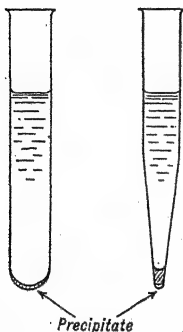


Fig. II, 3, 7

To remove the supernatant liquid, a capillary dropper is generally used. The centrifuge tube is held at an angle in the left hand, the rubber teat or nipple of the capillary dropper, held in the right hand, is compressed to expel the air and the capillary end is lowered into the tube until it is just below the liquid (Fig. II, 3, 8). As the pressure is *very slowly* released the liquid rises in the dropper and the latter is lowered further into the liquid until all the liquid is removed. Great care should be taken as the capillary approaches the bottom of the centrifuge tube that the tip does not touch the precipitate. The solution in the dropper should be perfectly clear: it can be transferred to

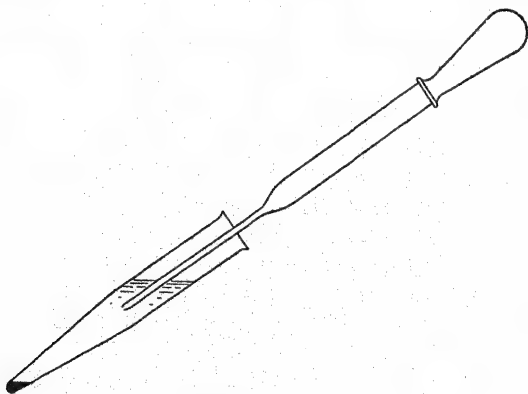


Fig. II, 3, 8

another vessel by merely compressing the rubber bulb. In difficult cases, a little cotton wool may be inserted in the tip of the dropper and allowed to protrude about 2 mm. below the glass tip; any excess of cotton wool should be cut off with scissors.

**6. Washing of precipitates.** It is essential to wash all precipitates in order to remove the small amount of solution

present in the precipitate, otherwise it will be contaminated with the ions present in the centrifugate. It is best to wash the precipitate at least twice, and to combine the first washing with the centrifugate. The wash liquid is a solvent which does not dissolve the precipitate but dilutes the quantity of mother liquor adhering to it. The wash liquid is usually water, but may be water containing a small amount of the precipitant (common ion effect) or a dilute solution of an electrolyte (such as an ammonium salt) since water sometimes tends to produce colloidal solutions, *i.e.* to peptise the precipitate.

To wash a precipitate in a centrifuge tube, 5–10 drops of water or other reagent are added and the mixture thoroughly stirred (stirring rod or platinum wire); the centrifuge tube is then counterbalanced against another similar tube containing water to the same level and centrifuged. The supernatant liquid is removed by a capillary dropper, and the washing is repeated at least once.

**7. Wash bottles.** For most work in semimicro analysis a 30 or 60 ml. glass-stoppered bottle is a suitable container for

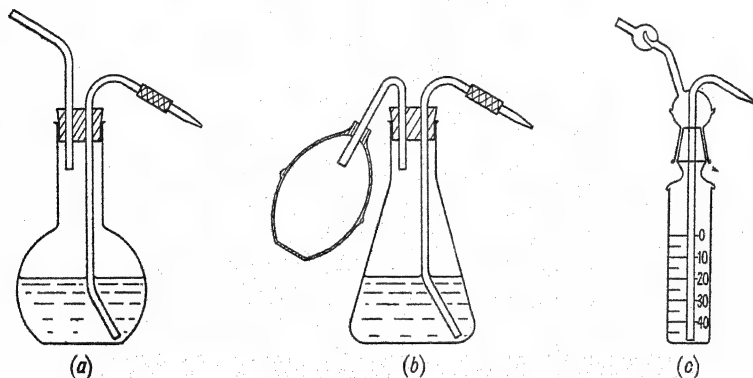


Fig. II, 3, 9

distilled water: the latter is handled with a reagent dropper. Alternatively, a bottle carrying its own dropper (Fig. II, 3, 4, *a* or *b*) may be used. A small conical flask (25 or 50 ml.) may be used for hot water. For those who prefer wash bottles, various types are available (Fig. II, 3, 9): *a* is a 100 or 250 ml. flat-bottomed flask with a jet of 0.5–1 mm. diameter, and is mouth-operated; *b* is a hand-operated wash bottle (flask, 125 ml.; rubber bulb, 50 ml.); and *c* is a Pyrex 50 ml. graduated wash bottle.

**8. Transferring of precipitates.** In some cases precipitates can be transferred from semimicro test-tubes with a small spatula (two convenient types in nickel or monel metal\* are shown in Fig. II, 3, 10). This operation is usually difficult, particularly for centrifuge tubes. Indeed, in semimicro analysis it is rarely necessary to transfer actual precipitates from one vessel to another. If, for some reason, transfer of the precipitate is essential, a wash liquid or the reagent itself is added, the mixture vigorously stirred and the resulting suspension transferred to a reagent dropper, and the contents of the latter ejected into the other vessel; if required, the liquid is removed by centrifugation.

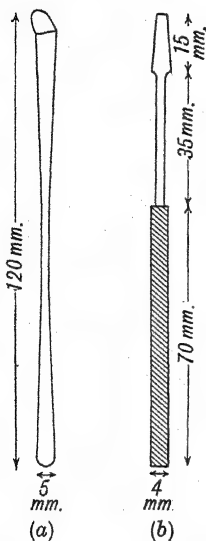


Fig. II, 3, 10

If the precipitate in a test-tube is to be treated with a reagent in an evaporating dish or crucible, the reagent is added first, the precipitate brought into suspension by agitation with a stirring rod, and the suspension is then poured into the open dish or crucible. The test-tube may be washed by holding it in an almost vertical (upside down) position with its mouth over the receptacle and

directing a fine stream of solution or water from a capillary dropper on to the sides of the test-tube.

**9. Heating of solutions.** Solutions in semimicro centrifuge tubes cannot be heated over a free flame owing to the serious danger of "bumping" (and consequent loss of part or all of the liquid) in such narrow tubes. The "bumping" or spattering of hot solutions may often be dangerous and lead to serious burns if the solution contains strong acids or bases. Similar remarks apply to semimicro test-tubes. However, by heating the side of the test-tube (8 ml.) and not the bottom alone with a micro burner, as indicated in Fig. II, 3, 11, and withdrawing from the flame periodically and shaking gently, "bumping" does not usually occur. The latter heating operation requires very careful manipulation and should not be attempted by elementary students. The mouth of the test-tube must be pointed away from the students nearby.

\* Type b, with slightly modified dimensions, is obtainable from Wilkens Anderson Co., 4525 W. Division Street, Chicago 51, Illinois, U.S.A.



The danger of "bumping" may be considerably reduced by employing the anti-bumping device shown in Fig. II, 2, 5; the tube should be about 1 cm. longer than the test-tube to facilitate removal.

On the whole it is better to resort to safer methods of heating. The simplest procedure is to employ a small water bath. This may consist of a 250 ml. Pyrex beaker, three-quarters filled with water and covered with a lead or galvanised iron plate (Fig. II, 3, 12) drilled with two holes to accommodate a test-tube and a centrifuge tube. It is a good plan to wind a thin

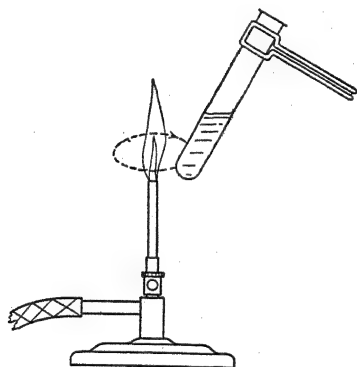


Fig. II, 3, 11

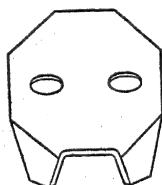


Fig. II, 3, 12

rubber band about 5 mm. from the top of the tube; this will facilitate the removal of the hot tube from the water bath without burning the fingers and, furthermore, the rubber band can be used for attaching small pieces of folded paper containing notes of contents, etc.

A more elaborate arrangement which will, however, meet the requirements of several students, is Barber's water bath rack (Fig. II, 3, 13). The dimensions of a rack of suitable size are given in Fig. II, 3, 14. This rack will accommodate four centrifuge tubes and four semimicro test-tubes. The apparatus is constructed of monel metal, stainless steel, a plastic material which is unaffected by water at 100°, or of brass which is subsequently tinned. The brass may be tinned by boiling with 20 per cent sodium hydroxide solution containing a few lumps of metallic tin.

**10. Evaporations.** Where rapid concentration of a liquid is required or where volatile gases must be expelled rapidly,

the semimicro boiling tube (*c* in Fig. II, 3, 1) may be employed. Two useful holders, constructed of a light metal alloy, are

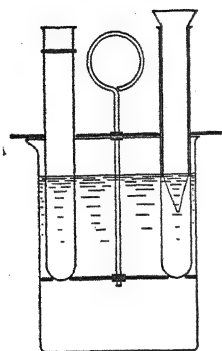


Fig. II, 3, 13

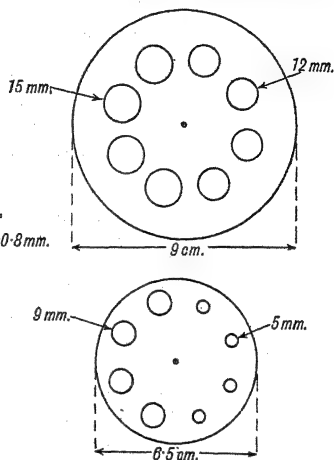
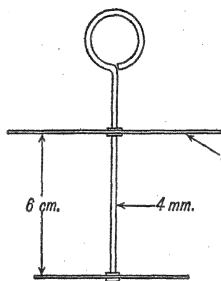


Fig. II, 3, 14

shown in Fig. II, 3, 15; *b* is to be preferred as the boiling tube cannot fall out by mere pressure on the holder at the point

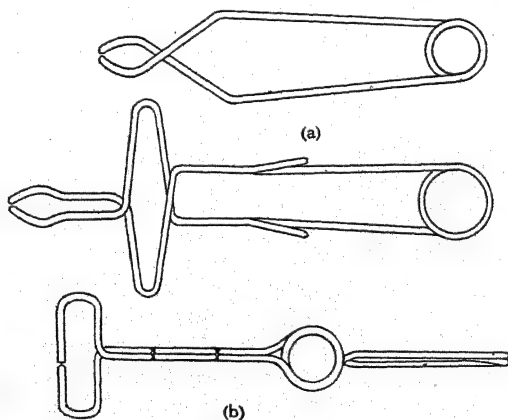


Fig. II, 3, 15

where it is usually held.\* Slow evaporation may be achieved by heating in a test-tube, crucible or beaker on a water bath.

\* A small wooden clothes-peg (spring type) may also be used for holding semimicro test-tubes.

If evaporation to dryness is required, a small casserole (*ca.* 6 ml.) or crucible (3–8 ml.) may be employed. This may be placed in an air bath consisting of a 30 ml. nickel crucible and supported thereon by an asbestos or uralite ring (Fig. II, 3, 16, *a*), and heated with a semimicro burner. Alternatively, a small Pyrex beaker (say, of 50 or 100 ml. capacity) may be used with a silica or nichrome triangle to support the crucible or casserole (Fig. II, 3, 16, *b*): this device may also be applied for evaporations in semimicro beakers.

Evaporation to dryness may also be accomplished by direct

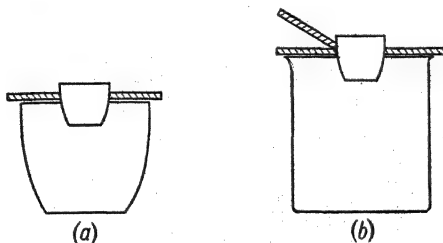


Fig. II, 3, 16

intermittent heating with a micro burner of a crucible (supported on a nichrome or silica triangle) or of a semimicro beaker (supported on a wire gauze). A little practice is required in order to achieve regular boiling by intermittent heating with a flame and also to avoid “bumping” and spattering: too hot a flame should not be used. In many cases the flame may be removed whilst a little liquid remains: the heat capacity of the vessel usually suffices to complete the evaporation without further heating. If corrosive fumes are evolved, the operation should be conducted in the fume cupboard.

**11. Dissolving of precipitates.** The reagent is added and the suspension is warmed, if necessary, on the water bath until the precipitate has dissolved. If only partial solution occurs, the suspension may be centrifuged.

**12. Precipitations with hydrogen sulphide.** Various automatic generators of the Kipp type are marketed, and may be employed for groups of students. Owing to the highly poisonous and very obnoxious character of hydrogen sulphide, these generators are always kept in a fume cupboard (draught chamber or hood). A wash bottle containing water should

always be attached to the generator in order to remove acid spray (compare Fig. II, 2, 1, *a*). The tube dipping into the liquid in the wash bottle should preferably be a heavy-walled capillary: this will give a better control of the gas flow and will also help to prolong the life of the charge in the  $\text{H}_2\text{S}$  generator.

Precipitation may be carried out in a centrifuge tube, but a semimicro test-tube or 10 ml. conical flask is generally preferred; for a large volume of solution, a 25 ml. Erlenmeyer flask may be necessary. The delivery tube is drawn out to a thick-walled capillary (1–2 mm. in diameter) and carries at the upper end a small rubber stopper which fits the semimicro test-tube\* (Fig. II, 3, 17) or conical flask. The perfectly clean delivery tube is connected to the source of hydrogen sulphide as in Fig. II, 2, 1 and a slow stream of gas is passed through the liquid for about 30 seconds in order to expel the air, the cork is pushed into position, and the passage of hydrogen sulphide is continued until very few bubbles pass through the liquid; the vessel is shaken gently from time to time. The tap in the gas generator is then turned off; the delivery tube is disconnected and immediately rinsed with distilled water. If the liquid must be warmed, the stopper is loosened, the vessel placed in the water bath for a few minutes, and the gas introduced again.

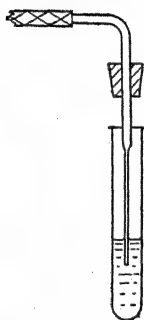


Fig. II, 3, 17

If an individual generator is desired, a Pyrex test-tube (150 × 20 mm.) charged with "Aitch-tu-ess" or an equivalent mixture (essentially an intimate mixture of a solid paraffin hydrocarbon, sulphur and asbestos) is utilised: this yields hydrogen sulphide when heated by a micro burner and the evolution of gas ceases (but not usually abruptly) when the source of heat is removed. The test-tube type of generator is depicted in Fig. II, 3, 18, *a*. The small hole (vent) is covered with the finger during the passage of the gas. Since the hydrogen sulphide evolution does not cease abruptly with the removal of the flame, an absorption bottle (Fig. II, 3, 18, *b*) is generally employed to absorb the unused gas. It consists of a 60 ml. bottle containing 10 per cent sodium hydroxide solution: the lower end of the longer 6 mm. tube is just above the surface

\* For a 3 ml. centrifuge tube or a 4 ml. test-tube, the top part of the rubber test (bulb) from a dropper makes a satisfactory stopper: a small hole is made in the rubber bulb and the delivery tube is carefully pushed through it.

of the solution. When saturation of the solution with the gas is completed, the capillary pipette and cotton wool bulb are removed and the absorption bottle is attached. The

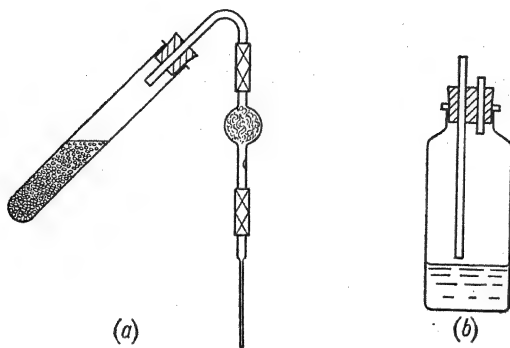


Fig. II, 3, 18

method is not strongly recommended because "pressure" precipitation (compare Section II, 2, 7) is difficult and, if attempted, introduces an element of danger.

**13. Identification of gases.** Many anions (*e.g.* carbonate, sulphide, sulphite, thiosulphate and hypochlorite) are usually identified by the volatile decomposition products obtained

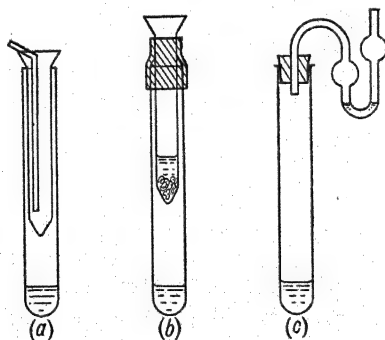


Fig. II, 3, 19

with the appropriate reagents. Suitable apparatus for this purpose are shown in Fig. II, 3, 19. The simplest form *a* consists of a semimicro test-tube with the accompanying "filter

tube"\*: a strip of test paper (or of filter paper moistened with the necessary reagent) about 3–4 mm. wide is suspended in the "filter tube." In those cases where spray is likely to affect the test paper, a loose plug of cotton wool should be placed at the narrow end of the "filter tube." Apparatus *b* is employed when the test reagent is a liquid. A short length of wide-bore rubber tubing is fitted over the mouth of a semimicro test-tube

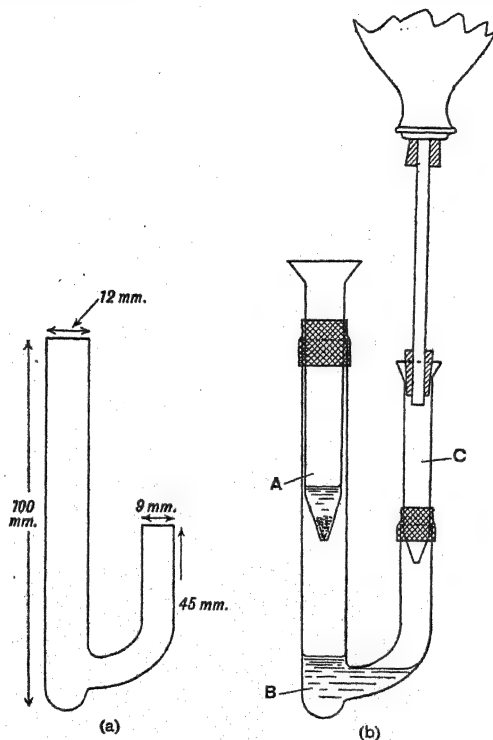


Fig. II, 3, 20

with about 1 cm. protruding over the upper edge. The chemical reaction is started in the test-tube and a "filter tube" containing a tightly-packed plug of cotton wool is inserted through the rubber collar, the filter plug again packed down with a 4 mm. glass rod, and 0.5–1 ml. of the reagent introduced. An

\* Test-tubes (75 × 10 mm. and 100 × 12 mm.) together with the matching "filter tubes" (55 × 7 mm. and 80 × 9 mm.) are standard Pyrex products; they are inexpensive and therefore eminently suitable for elementary and other students. The smaller size is satisfactory for most purposes.

alternative apparatus for liquid reagents is shown in *c*: it is a type of absorption pipette and is attached to the 4 ml. test-tube by a rubber stopper or a tightly-fitting paraffined cork. A drop or two of the liquid reagent is introduced into the absorption tube. The double bulb ensures that all the evolved gas reacts, and it also prevents the test reagent from being sucked back into the reaction mixture. All the above apparatus, *a-c*, may be warmed by placing in the hot water rack (*e.g.* Fig. II, 3, 13). They will meet all normal requirements for testing gases evolved in reactions in qualitative analysis.

When the amounts of evolved gas are likely to be small, the apparatus of Fig. II, 3, 20 may be used: all the evolved gas may be swept through the reagent by a stream of air introduced by a rubber bulb of 3-4 fluid ounces capacity.\* The approximate dimensions of the essential part of the apparatus are given in *a*, whilst the complete assembly is depicted in *b*. The sample under test is placed in B, the test reagent is introduced into the "filter tube" A over a tightly-packed plug of cotton wool (or other medium), and the acid or other liquid reagent is added through the "filter tube" C. The rubber bulb is inserted into C, and by depressing it gently air is forced through the apparatus, thus sweeping out the gases through the test reagent in A. The apparatus may be warmed by placing it in a hot water bath.

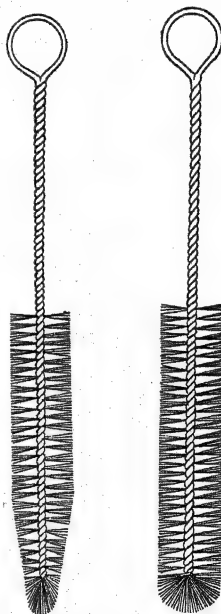


Fig. II, 3, 21

**14. Cleaning of apparatus.** It is essential to keep all apparatus scrupulously clean if trustworthy results are to be obtained. All apparatus must be thoroughly cleaned with cleaning mixture (a solution of sodium dichromate in concentrated sulphuric acid, say 70 g.  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  per litre) or with a brush and cleaning powder. The apparatus is then rinsed several times with tap water, and repeatedly with distilled water. Special brushes (Fig. II, 3, 21) are available for semimicro test-tubes and centrifuge tubes; the

\* The bulb of a commercial rectum or ear syringe is satisfactory.

commercial "pipe cleaners" are also satisfactory. The tubes may be allowed to drain in a special stand or else they may be inverted in a small beaker on the bottom of which there are several folds of filter paper or a filter paper pad to absorb the water. Larger apparatus may be allowed to drain on a clean linen towel or glass cloth. Droppers are best cleaned by first removing the rubber bulbs or teats and allowing distilled water to run through the tubes; the teats are cleaned by repeatedly filling them with distilled water and emptying them. When clean, they are allowed to dry on a linen glass cloth. At the end of the laboratory period, the clean apparatus is placed in a box with cover, so that they may remain clean until required.

**15. Spot plates. Drop reaction paper.** These are employed chiefly for confirmatory tests (see Section II, 6 for a full discussion). Spot plates with a number of circular cavities are marketed, either black or white. The former are employed for white or light-coloured precipitates, and the latter for dark-coloured precipitates. Transparent spot plates (*e.g.* Jena) and combination black and white spot plates (with line of demarcation between the black and white running exactly through the centres of the depressions) are also available commercially. Spot plates are useful for mixing small quantities of reagents, and also for testing the  $pH$  of a solution colorimetrically.

Drop reaction or spot test paper (*e.g.* Whatman, No. 120) is a soft variety of pure, highly porous paper which is used for reactions that result in highly coloured precipitates. The precipitate does not spread very far into the paper because of the filtering action of the pores of the paper; consequently the spot test technique is employed in highly sensitive identification tests, the white paper serving as an excellent background for dark or highly coloured precipitates, and incidentally providing a permanent record of the test.

Semi-quantitative results may be obtained by the use of the Yagoda "confined-spot-test" papers (Schleicher and Schuell, U.S.A., Nos. 211Y and 597Y): these are prepared with a chemically inert, water-repelling barrier which constricts the spot reaction to a uniform area of fixed dimensions.

**16. Calculation of the volume of precipitating reagents.** This type of calculation is instructive, for it will assist the student to appreciate fully the significance of the quantities of reagent employed in semimicro analysis. Let us assume that a sample contains 1 mg. of silver ions and 2 mg. of mercurous



ions, and that the precipitating agent is 5*N* hydrochloric acid. To calculate the volume of the precipitating agent required, the number of equivalents of the ion or ions to be precipitated and the number of equivalents per ml. of the precipitating agent must be ascertained. In the present sample there will be  $(1 \times 10^{-3})/107.9 = 9.3 \times 10^{-6}$  equivalents of silver ion and  $(2 \times 10^{-3})/200.6 = 1 \times 10^{-5}$  equivalents of mercurous ion, *i.e.* the total concentration of cation is  $1.93 \times 10^{-5}$  equivalents. Now 1 ml. of 5*N* hydrochloric acid contains  $5 \times 10^{-3}$  equivalents of chloride ion, so that the volume of acid required will be  $(1.93 \times 10^{-5})/(5 \times 10^{-3}) = 0.0039$  ml. The capillary dropper delivers a drop of about 0.03 ml. (30–40 drops per ml.), hence 1 drop of 5*N* hydrochloric acid contains sufficient chloride ions to precipitate the silver and mercurous ions and also to provide a large excess to reduce the solubility of the sparingly soluble chlorides (common ion effect).

In practice, the weights of the ions in a solution of the sample are usually not known, so that exact calculations cannot be made. However, if the weight of sample employed is known, the maximum amount of precipitating agent required can be easily calculated. This is one of the reasons for taking a known weight (weighed to the nearest milligram) of the sample for analysis. Let us consider an actual example. We may assume that 50 mg. of the solid sample or, for solutions, such a volume as will yield 50 mg. of solid upon evaporation to dryness, is taken for analysis and that the maximum quantity of all the metal ions present in the sample is 35 mg. It is evident that the smaller the equivalent of a given ion, the greater will be the number of equivalents contained in a given weight of it and hence the larger the volume of hydrochloric acid required for precipitation. In Group I, lead has the lowest equivalent (103.5). The number of equivalents for 35 mg. of lead is  $35/(103.5 \times 1000) = 3.38 \times 10^{-4}$  equivalents or 0.338 milli-equivalents. Now 1 ml. of 5*N* hydrochloric acid contains  $5 \times 10^{-3}$  equivalents or 5 milli-equivalents. Hence the exact volume of this acid required for complete precipitation is  $0.338/5 = 0.0676$  ml. = 2 drops, and the addition of 3–4 drops will suffice for complete precipitation (common ion effect) and also to prevent the precipitation of bismuth and antimony oxychlorides.

### 17. Some practical hints (compare Section II, 2, 14):

(1) Upon commencing work, arrange the more common and frequently used apparatus in an orderly manner on your bench.

Each item of apparatus should have a definite place so that it can be found readily when required. All apparatus should have been cleaned during the previous laboratory period.

(2) Weigh the sample for analysis (if a solid) to the nearest milligram: 50 mg. is a suitable quantity.

(3) Read the laboratory directions carefully and be certain that you understand the purpose of each operation—addition of reagents, etc. Examine the label on the bottle *before* adding the reagent. Serious errors leading to a considerable loss of time and, possibly, personal injury may result from the use of the wrong reagent. Return each reagent bottle to its proper place *immediately* after use.

(4) When transferring a liquid reagent with a reagent dropper, always hold the dropper just above the mouth of the vessel and allow the reagent to “drop” into the vessel. Do not allow the dropper tip to touch anything outside the reagent bottle; the possible introduction of impurities is thus avoided. Similar remarks apply to the use of T.K. dropper bottles.

(5) Never dip your own dropper into a reagent. Pour a *little* of the reagent (e.g. a corrosive liquid) into a small clean vessel (test-tube, crucible, beaker, etc.) and introduce your dropper into this. Never return the reagent to the bottle; it is better to waste a little of the reagent than to take the risk of contaminating the whole supply.

(6) Do not introduce your spatula into a reagent bottle to remove a little solid. Pour or shake a little of the solid on to a clean, dry watch glass, and use this. Do not return the solid reagent to the stock bottle. Try and estimate your requirements and pour out only the amount necessary.

(7) All operations resulting in the production of fumes (acid vapours, volatile ammonium salts, etc.) or of poisonous or disagreeable gases (hydrogen sulphide, chlorine, sulphur dioxide, etc.) must be performed in the fume chamber.

(8) Record your observations briefly in your note-book in ink *immediately* after each operation has been completed.

(9) Keep your droppers scrupulously clean. Never place them on the bench. Rinse the droppers several times with distilled water after use. At the end of each laboratory period, remove the rubber teat or cap and rinse it thoroughly.

(10) During the course of the work place dirty centrifuge tubes, test-tubes, etc., in a definite place, preferably in a beaker, and wash them at convenient intervals. This task can often be done while waiting for a solution to evaporate or for a precipitate to dissolve while being heated on a water bath.

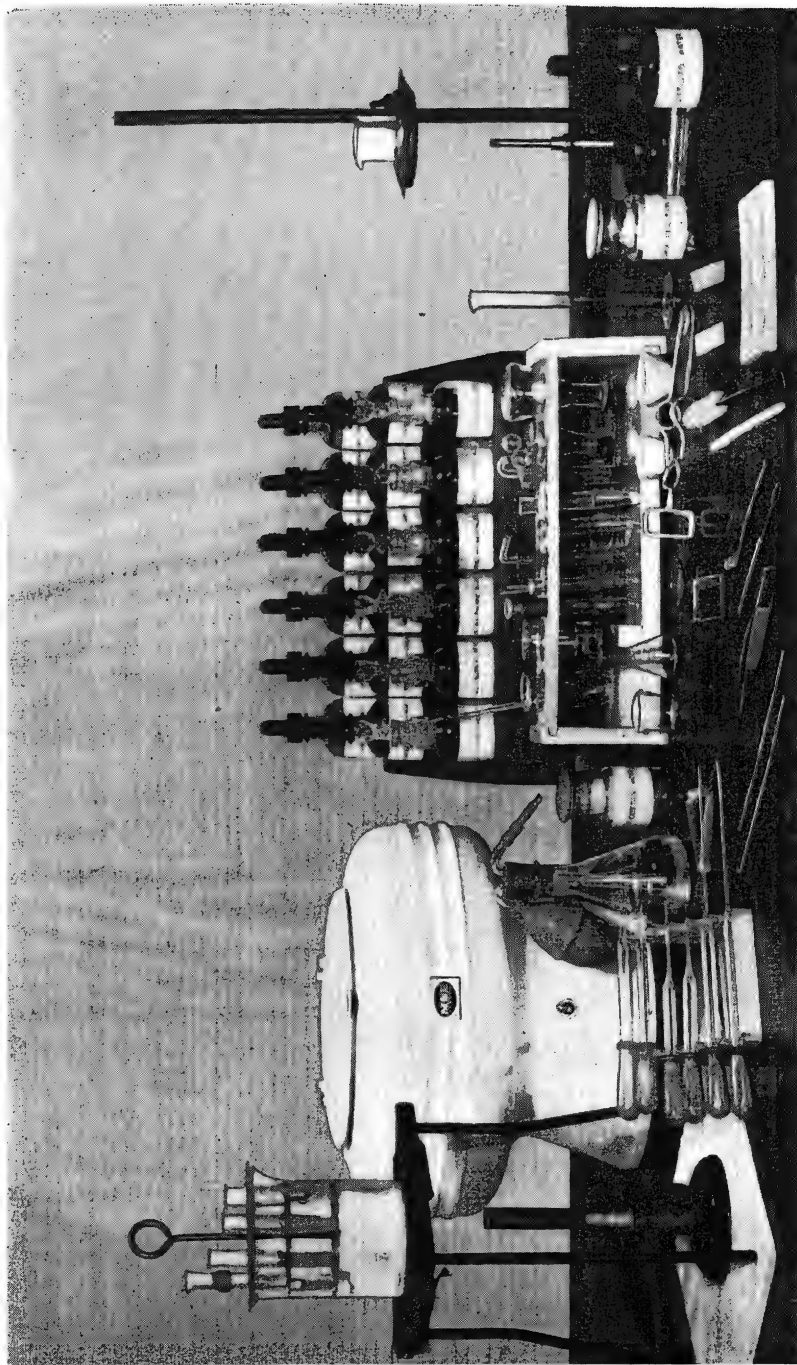
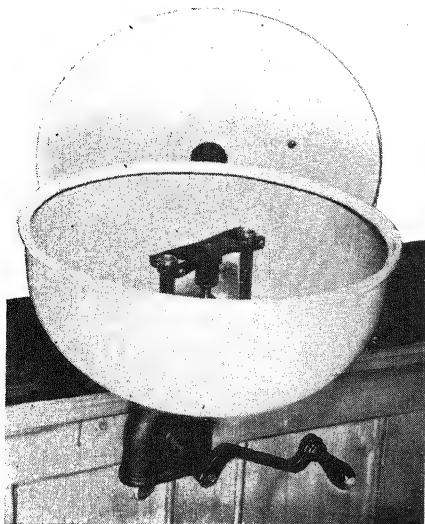


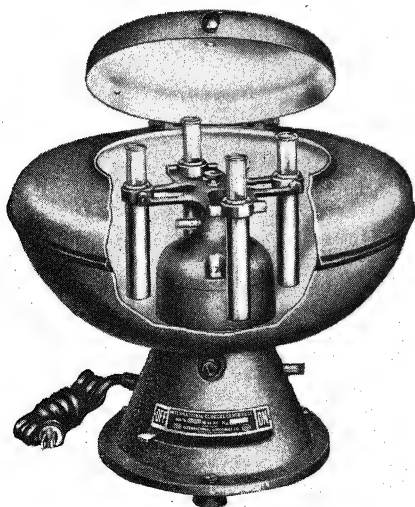
Fig. II, 3, 22. SEMIMICRO APPARATUS



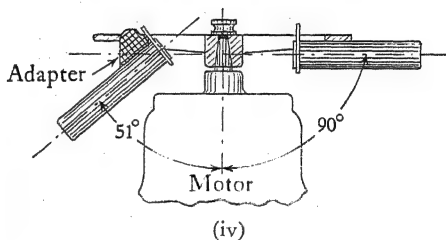
(i)



(ii)



(iii)



- (i) HAND CENTRIFUGE (*Moseley*)
  - (ii) ELECTRIC CENTRIFUGE (*International*, "micro")
  - (iii) ELECTRIC CENTRIFUGE (*International*, "clinical")
- Note.* The British equivalents of (ii) and (iii) are the M.S.E. "micro" and "minor" respectively.
- (iv) Rubber Adapter to convert (ii) for angle sedimentation (*diagrammatic*)

(11) Adequately label all solutions and precipitates which must be carried over to the next laboratory period.

(12) When in difficulty, or if you suspect any apparatus (*e.g.* the centrifuge) is not functioning efficiently, consult the teacher.

**18. Semimicro apparatus.** The plates (Figs. *II*, 3, 22 and *II*, 3, 23) show all the general apparatus required for semimicro analysis. Other apparatus of specialised character will be described in the text.

The apparatus suggested for each student is listed below (see plate, Fig. *II*, 3, 22). (The liquid reagents recommended for each student are given in Section *II*, 3, 4.)

- 1 beaker, Pyrex, Griffin form, 250 ml.
- 1 hot water rack constructed of tinned copper (Fig. *II*, 3, 13-14) or
- 1 lead cover (Fig. *II*, 3, 12) for water bath.
- 1 beaker, Pyrex, 5 ml.
- 1 beaker, Pyrex, 10 ml.
- 1 conical flask, Pyrex, 100 ml., and one 50 ml. rubber bulb (for wash bottle, Fig. *II*, 3, 9, *b*).
- 2 conical flasks, Pyrex, 10 ml.
- 1 conical flask, Pyrex, 25 ml.
- 6 test-tubes, Pyrex, 75 × 10 mm.,\* 4 ml., with rim.
- 2 test-tubes, Pyrex, 75 × 10 mm.,\* 4 ml., without rim.
- 2 "filter tubes," Pyrex, 55 × 7 mm.\* (Fig. *II*, 3, 19, *a*).
- 1 gas absorption pipette (with 75 × 10 mm. test-tube and rubber stopper, Fig. *II*, 3, 19, *c*).
- 4 centrifuge tubes, Pyrex, 3 ml. (Fig. *II*, 3, 1, *d*).
- 2 semimicro boiling tubes, Pyrex, 60 × 25 mm., 20 ml.
- 1 wooden stand (to house test-tubes, "filter tubes," gas absorption pipette, conical flasks, *etc.*).
- 2 medicine droppers, complete with rubber teats (bulbs).
- 2 reagent droppers (Fig. *II*, 3, 3, *a*).
- 2 capillary droppers (Fig. *II*, 3, 3, *b*).
- 1 stand for droppers.
- 2 anti-bump tubes (Fig. *II*, 2, 5).
- 1 crucible, porcelain, Royal Worcester, 3 ml. (23 × 15 mm.).
- 1 crucible, porcelain, Royal Worcester, 6 ml. (28 × 20 mm.).
- 1 crucible, porcelain, Royal Worcester, 8 ml. (32 × 19 mm.).
- 3 rubber stoppers (one  $\frac{3}{8} \times \frac{1}{2}$  inch, two  $\frac{1}{4} \times \frac{5}{8}$  inch, to fit 25 ml. conical flask, test-tube and gas absorption pipette).
- 30 cm. glass tubing, 4 mm. outside diameter (for H<sub>2</sub>S apparatus).

\* Semimicro test-tubes (Pyrex, 100 × 12.5 mm., 8 ml.) and the appropriate "filter tubes" (Pyrex, 80 × 9 mm.) are marketed, and these may find application in analysis. The smaller 4 ml. test-tubes will generally suffice; their great advantage is that they can be used directly in a semimicro centrifuge in the buckets provided for the 3 ml. centrifuge tubes.

- 10 cm. rubber tubing, 3 mm. (for  $H_2S$  apparatus).
- 5 cm. rubber tubing, 5 mm. (for "filter tubes").
- 30 cm. glass rod, 3 mm. (for stirring rods, Fig. II, 3, 2).
- 1 measuring cylinder, 5 ml.
- 1 watch glass,  $1\frac{1}{2}$  inch diameter.
- 2 cobalt glasses,  $1\frac{1}{2} \times 1\frac{1}{2}$  inches.
- 2 microscope slides.
- 1 platinum wire (5 cm. of 0.3 mm. diameter).
- 1 forceps, 4 inches.
- 1 semimicro spatula (Fig. II, 3, 10, *a* or *b*).
- 1 semimicro test-tube holder (Fig. II, 3, 15).
- 1 semimicro test-tube brush (Fig. II, 3, 21).
- 1 pipe cleaner.
- 1 spot plate (6 cavities).
- 1 wide-mouthed bottle, 1 ounce, filled with cotton wool.
- 1 wide-mouthed bottle, 1 ounce, filled with strips ( $2 \times 2$  cm.) of drop reaction paper.
- 1 dropping bottle, labelled DISTILLED WATER.
- 1 packet blue litmus paper.
- 1 packet red litmus paper.
- 1 triangular file (small).
- 1 tripod and wire gauze (for water bath).
- 1 retort stand and one iron ring (3 inches).
- 1 wire gauze (for ring).
- 1 triangle, silica.
- 1 triangle, nichrome.
- 1 burner, Bunsen or Tirrill.
- 1 semimicro burner.

## TECHNIQUE OF MICRO ANALYSIS

**II, 4. General Discussion.**—In micro analysis the scale of operations as compared with macro analysis is reduced by a factor of 0.01. Thus whereas in macro analysis the weights and volumes for analysis are 0.5–1 g. and about 10 ml., and in semimicro analysis 50 mg. and 1 ml. respectively, in micro analysis the corresponding quantities are about 5 mg. and 0.1 ml. Micro analysis is sometimes termed milligram analysis to indicate the order of weight of the sample employed. It must be pointed out that whilst the weight of the sample for analysis has been reduced, the ratio of weight to volume has been retained and in consequence the concentration of the individual ions, *etc.*, are maintained. A special technique must be used for handling such small quantities of materials. There is no sharp line of demarcation between semimicro and micro analysis and much of the technique described for the former can, with suitable modifications to allow for the reduction in scale by about one-tenth, be utilised for the latter. Some of the modifications, involving comparatively simple apparatus, will be described. No

attempt will be made to deal with operations centered round the microscope (magnification up to 250) as the specialised technique is outside the scope of this volume.\*

The small amounts of material obtained after the usual systematic separations can be detected, in many cases, by what is commonly called **spot analysis**, *i.e.* analysis which utilises spots of solutions (about 0.05 ml. or smaller) or a fraction of milligram of solids. Spot analysis has been developed as a result of the researches of numerous chemists: the names of Tananaeff, Krumholz, Wenger, van Nieuwenburg, Gutzeit and, particularly, Feigl and their collaborators must be mentioned in this connexion. In general, spot reactions are preferable to tests which depend upon the formation and recognition of crystals under the microscope, in that they are easier and quicker to carry out, less susceptible to slight variations of experimental conditions, and can be interpreted more readily. Incomplete schemes of qualitative inorganic analysis have been proposed which are based largely upon spot tests: these cannot, however, be regarded as entirely satisfactory for very few spot tests are specific for particular ions and also the adoption of such schemes will not, in the long run, help in the development of micro qualitative analysis. Furthermore, such schemes, when considered from the point of view of training of students in the theory and practice of analysis, are pedagogically unsound. It seems to the writer that the greatest potential progress lies in the use of the common macro procedures (or simple modifications of them) to effect the preliminary separations for which the specialised micro technique is adopted, followed by the utilisation of spot tests *after* the group or other separation has been effected. Hence the following pages will contain an account of the methods which can be used for performing macro operations on a micro scale and also to a discussion of the technique of spot analysis.

## II, 5. Micro Apparatus and Micro Analytical Operations.—

It is assumed that the reader is familiar with the account of semi-micro technique given in Section II, 3.

**Micro centrifuge tubes** (Fig. II, 5, 1) of 0.5–2 ml. capacity† replace test-tubes, beakers and flasks for most operations. Two types of centrifuge tubes are shown: *b* is particularly useful when

\* For a detailed account, see E. M. Chamot and C. W. Mason, *Handbook of Chemical Microscopy*, Volume I (1938) and Volume II (1940) (J. Wiley; Chapman and Hall); also A. A. Benedetti-Pichler, *Introduction to the Micro-technique of Inorganic Analysis* (1942) (J. Wiley; Chapman and Hall).

† The dimensions given ensure that the centrifuge tubes fit into the buckets of a semimicro centrifuge. The dimensions for other capacities are: Type *a*: 0.5 ml., 60 × 6.3 mm. (ext.); 2 ml., 68 × 11.25 mm. (ext.); 3 ml., 76 × 11.25 mm. (ext.). Type *b*: 0.5 ml., 63 mm., 8.5 mm. (ext.), 2.5 mm. (int.).

All the dimensions have been extracted from B.S. 1428, 1953, Micro-chemical Apparatus, Part E3, Micro-centrifuge Accessories, and are reproduced by kind permission of British Standards Institution, 24 Victoria Street, London, S.W.1.

very small amounts of precipitate are being handled. Centrifuge tubes are conveniently supported in a rack consisting of a wooden block provided with 6 to 12 holes, evenly spaced, of  $\frac{5}{8}$  inch diameter and  $\frac{1}{2}$  inch deep.

Solutions are separated from precipitates by centrifuging. Semi-micro centrifuges (Section II, 3, 5), either hand-operated or electrically - driven, can be used. Adapters are provided inside the buckets (baskets) in order to accommodate micro centrifuge tubes with narrow open ends.

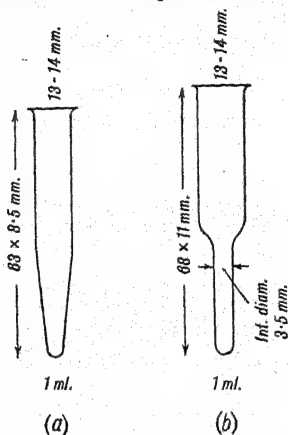


Fig. II, 5, 1

**Precipitations** are usually carried out in micro centrifuge tubes. After centrifuging, the precipitate collects in the bottom of the tube. The supernatant liquid may be removed either by a capillary dropper (Fig. II, 3, 3) or by means of a **transfer capillary pipette**. The latter consists of a thin glass tube (internal diameter about 2 mm.: this can be prepared from wider tubing) 20 to 25 cm. in length with one end drawn out in a micro flame to a tip with a fine opening. The correct method of

transferring the liquid to the capillary pipette will be evident from Fig. II, 5, 2. The centrifuge cone is held in the right hand and the capillary pipette is pushed slowly towards the precipitate so that the point of the capillary remains just below the surface of the liquid. As the liquid rises in the pipette, the latter is gradually lowered, always keeping the tip just below the surface of the liquid

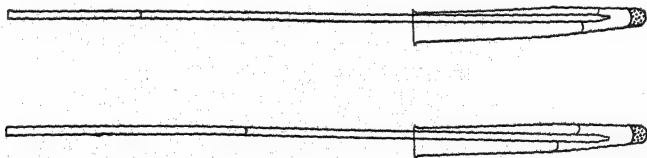


Fig. II, 5, 2

until the entire solution is in the pipette and the tip is about 1 mm. above the precipitate. The pipette is removed and the liquid blown or drained out into a clean dry centrifuge tube.

Another useful method for **transferring the centrifugate** to, say, another centrifuge tube will be evident upon reference to Fig. II, 5, 3. The siphon is made of thermometer capillary and is attached to the capillary pipette by means of a short length of rubber tubing



of 1 mm. bore. The small hole A in the side tube permits of perfect control of the vacuum; the side arm of the small test-tube is situated near the bottom so as to reduce spattering of the liquid in the centrifuge tube inside the test-tube when the vacuum is released. Only

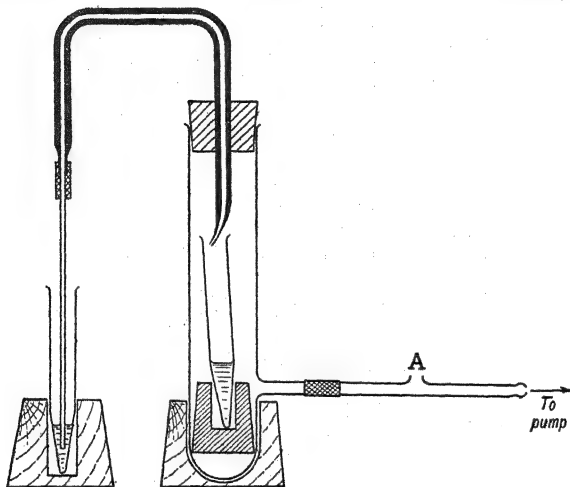
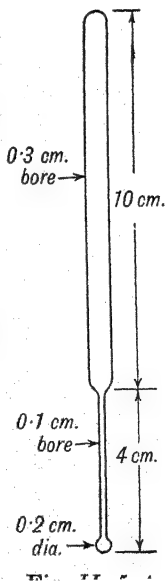


Fig. II, 5, 3

gentle suction is applied and the opening A is closed with the finger; upon removing the finger, the action of the capillary siphon ceases immediately.

For the washing of precipitates the wash solution is added directly to the precipitate in the centrifuge tube and stirred thoroughly either by a platinum wire or by means of a micro stirrer, such as is shown in Fig. II, 5, 4; the latter can readily be made from thin glass rod. The mixture is then centrifuged, and the clear solution removed by a transfer capillary pipette as already described. It may be necessary to repeat this operation two or three times to ensure complete washing.

The transfer of precipitates is comparatively rare in micro qualitative analysis. Most of the operations are usually so designed that it is only necessary to transfer solutions. However, if transfer of a precipitate should be essential and the precipitate is crystalline, the latter may be sucked up by a dry dropper pipette and transferred to the appropriate vessel. If the precipitate



is gelatinous, it may be transferred with the aid of a narrow glass, nickel, monel metal or platinum spatula. The centrifuge tube must be of type *a* (Fig. II, 5, 1) if most of the precipitate is to be removed.

The heating of solutions in centrifuge tubes is best carried out by supporting them in a suitable stand (compare Figs. II, 3, 12-13) and heating on a water bath. When higher temperatures are

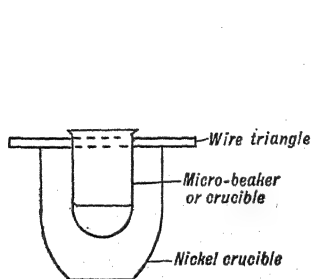


Fig. II, 5, 5

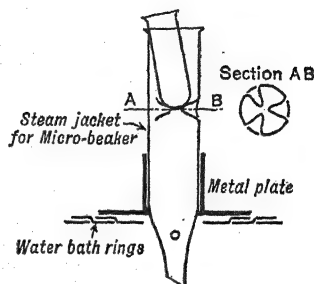


Fig. II, 5, 6

required, as for evaporation, the liquid is transferred to a micro beaker or micro crucible; this is supported by means of a nichrome wire triangle as indicated in Fig. II, 5, 5. Micro beakers may be heated by means of the device shown in Fig. II, 5, 6, which is laid on a water bath.

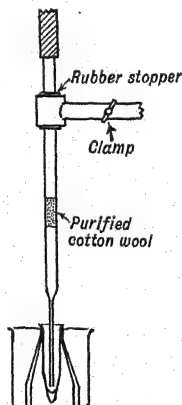


Fig. II, 5, 7

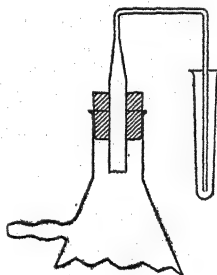


Fig. II, 5, 8

Another valuable method for concentrating solutions or evaporating to dryness directly in a centrifuge tube consists in conducting the operation on a water bath in a stream of filtered air supplied through a capillary tube fixed just above the surface of the liquid. The experimental details will be evident by reference to Fig. II, 5, 7.

Micro centrifuge tubes are cleaned with a feather, "pipe cleaner" or small test-tube brush (compare Fig. II, 3, 21). They are then filled with distilled water and emptied by suction as in Fig. II, 5, 8. After suction has commenced and the liquid removed, the tube is filled several times with distilled water without removing the suction device. Dropper pipettes are cleaned by repeatedly filling and emptying them with distilled water, finally separating rubber bulb and glass tube, and rinsing both with distilled water from a wash bottle. A transfer capillary pipette is cleaned by blowing a stream of water through it.

The passage of hydrogen sulphide into a solution in a micro centrifuge tube is carried out by leading the gas through a fine capillary tube in order not to blow the solution out of the tube. The delivery tube may be prepared by drawing out part of a length of glass tubing of 6 mm. diameter to a capillary of 1-2 mm. bore and 10-20 cm. long. A plug of pure cotton wool is inserted into the wide part of the tubing, and then the capillary tube is drawn out by means of a micro burner to a finer tube of 0.3-0.5 mm. bore and about 10 cm. long. The complete arrangement is illustrated in Fig. II, 5, 9.

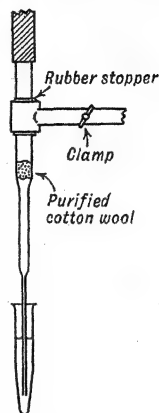


Fig. II, 5, 9

Such a fine capillary delivers a stream of very small bubbles of gas: large bubbles would throw the solution out of the micro centrifuge tube. The flow of the hydrogen sulphide must be commenced before introducing the point of the capillary into the centrifuge cone. If this is not done, the solution will rise in the capillary and when hydrogen sulphide is admitted, a precipitate will form in the capillary tube and clog it. The point of saturation of the solution is indicated by an increase in the size of the bubbles; this is usually after about two minutes.

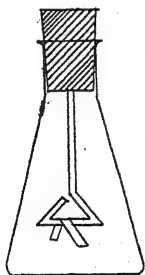


Fig. II, 5, 10

The identification of gases obtained in the reactions for anions may be conducted in an Erlenmeyer (or conical) flask of 5 or 10 ml. capacity; it is provided with a rubber stopper which carries at its lower end a "wedge point" pin, made preferably of nickel or monel metal (Fig. II, 5, 10). A small strip of impregnated test paper is placed on the loop of the pin. The stoppered flask, containing the reaction mixture and test paper is placed on a water bath for five minutes. An improved apparatus consists of a small flask provided with a ground glass stopper on to which a glass hook is fused (compare Fig. II, 6, 12): the test paper is suspended from the glass hook. If the evolved gas is to be passed through a liquid reagent, the apparatus

of Fig. II, 3, 19, *b* or *c*, proportionately reduced, may be employed.

**Confirmatory tests** for ions may be carried out either on drop reaction paper or upon a spot plate. The technique of spot tests is fully described in Section II, 6.

The following **micro apparatus\*** will be found useful:

- (1) Micro porcelain, silica and platinum crucibles of 0.5 to 2 ml. capacity.
- (2) Micro beakers (5 ml.) and micro conical flasks (5 ml.).
- (3) Micro centrifuge tubes, (0.5, 1.0 and 2.0 ml.).
- (4) Micro test-tubes ( $40-50 \times 8$  mm.).
- (5) Micro volumetric flasks (1, 2 and 5 ml.).
- (6) Micro nickel, monel or platinum spatula, 7-10 cm. in length and flattened at one end.
- (7) Micro burner.
- (8) Micro agate pestle and mortar.
- (9) Magnifying lens,  $5\times$  or  $10\times$ .
- (10) A pair of small forceps.
- (11) A small platinum spoon, capacity 0.5-1 ml., with handle fused into a glass tube. (This may be used for fusions.)

**II, 6. Apparatus required for Spot Test Analysis.**—The term “spot reaction” is applied to micro and semimicro tests for compounds or for ions. In these chemical tests manipulation with drops (macro, semimicro and micro) play an important part. Spot reactions may be carried out by any of the following processes:

- (i) By bringing together one drop of the test solution and of the reagent on porous or non-porous surfaces (paper, glass or porcelain).
- (ii) By placing a drop of the test solution on an appropriate medium (*e.g.* filter paper) impregnated with the necessary reagents.
- (iii) By subjecting a strip of reagent paper or a drop of the reagent to the action of the gases liberated from a drop of the test solution or from a minute quantity of the solid substance.
- (iv) By placing a drop of the reagent on a small quantity of the solid sample, including residues obtained by evaporation or ignition.
- (v) By adding a drop of the reagent to a small volume (say, 0.5-2 ml.) of the test solution and then extracting the reaction products with organic solvents.

The actual “spotting” is the fundamental operation in spot test analysis, but it is not always the only manipulation involved. Preliminary preparation is usually necessary to produce the correct reaction conditions. The preparation may involve some of the operations of macro analysis on a diminished scale (compare Section II, 5), but it may also utilise certain operations and apparatus peculiar to spot test analysis. An account of the latter forms the subject matter of the present Section.

Before dealing with the apparatus required for spot test reactions,

\* All glass apparatus must be of resistance (*e.g.* Pyrex) glass.

it is necessary to define clearly the various terms which are employed to express the sensitivity of a test. The **limit of identification** is the smallest amount recognisable, and is usually expressed in **micro grams** ( $\mu\text{g.}$ ) or **gamma** ( $\gamma$ ), one micro gram or one gamma being one-thousandth part of a milligram or one-millionth part of a gram.

$$1 \mu\text{g.} = 1\gamma = 0.001 \text{ mg.} = 10^{-6} \text{ g.}$$

Throughout this text the term **sensitivity** will be employed synonymously with limit of identification. The **concentration limit** is the greatest dilution in which the test gives positive results; it is expressed as a ratio of substance to solvent or solution. For these two terms to be comparable, a standard size drop must be used in performing the test. Throughout this book, unless otherwise stated, sensitivity will be expressed in terms of a standard drop of 0.05 ml.

The removal and addition of drops of test and reagent solutions is most simply carried out by using glass tubing, about 20 cm. long and 3 mm. external diameter; drops from these tubes have an approximate volume of 0.05 ml. The capillary dropper (Fig. II, 3, 3, b) may also be employed. A useful glass pipette, about 20 cm. long, may be made from 4 mm. tubing and drawn out at one end in the flame (Fig. II, 6, 1); the drawn-out ends of these pipettes may be made of varying bores. A liberal supply of glass tubes and pipettes should always be kept at hand. They may be stored in a beaker about 10 cm. high with the constricted end downwards and resting upon a pad of pure cotton wool; the beaker and pipettes can be protected against dust by covering with a sheet of cellophane. Pipettes which are used frequently may be supported horizontally on a stand constructed of thin glass rod. After use, they should be immersed in beakers filled with distilled water: interchanges are thus prevented and subsequent thorough cleaning is facilitated.



Fig. II, 6, 1

One-third  
actual size

Very small and even-sized drops can be obtained by means of **platinum wire loops**; the size of the loop can be varied and by calibrating the various loops (by weighing the drops delivered), the amount of liquid delivered from each loop is known fairly accurately. A number of loops are made by bending platinum wire of suitable thickness; the wires should be attached in the usual manner to lengths of glass rod or tubing to act as handles. They are kept in Pyrex test-tubes fitted with corks or rubber stoppers and labelled with particulars of the size of drop delivered. It must be pointed out that new smooth platinum wire allows liquids to drop off too readily, and hence it is essential to roughen it by dipping into chloroplatinic acid solution, followed by heating to glowing in a flame; this should be repeated several times. Micro burettes sometimes find application for the delivery of drops.

Reagent solutions can be added from dropping bottles of 25–30 ml. capacity (see Section II, 3, 4). A stock bottle for water and for solutions which do not deteriorate on keeping, is shown in Fig. II, 6, 2; it permits the facile addition in drops. This stock bottle is constructed from a Pyrex flask into which a tube with a capillary end is fused; a small rubber bulb is placed over the drawn-out neck, which has a small hole to admit air.

**Digestion** of solid samples with acid or solvent may be performed in small crucibles heated on a metal hot plate, or in an air bath (Fig. II, 5, 5), or in the glass apparatus illustrated in Fig. II, 6, 3. The last-named is heated over a micro burner, and then rotated so that supernatant liquid or solution may be poured off drop-wise without danger or loss.

**Spot tests** may be performed in a number of ways: on a spot plate,

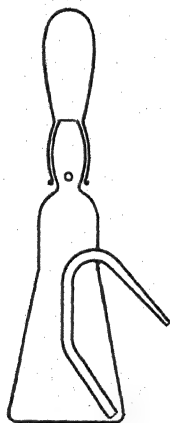


Fig. II, 6, 2  
One-third actual size

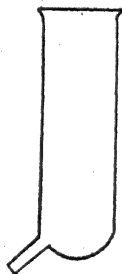


Fig. II, 6, 3  
Actual size

in a micro crucible, test tube or centrifuge tube, or on filter paper. Gas reactions are carried out in special apparatus.

The commercial **spot plates** are made from glazed porcelain and usually contain 6 to 12 depressions of equal size that hold 0.5 to 1 ml. of liquid. It is advisable, however, to have several spot plates with depressions of different sizes. The white porcelain background enables very small colour changes to be seen in reactions that give coloured products; the colour changes are more readily perceived by comparison with blank tests in adjacent cavities of the spot plate. Where light-coloured or colourless precipitates or turbidities are formed, it is better to employ black spot plates. Transparent spot plates of resistance glass (*e.g.* Jena) are also available; these may be placed upon glossy paper of suitable colour. The drops of test solution and reagent brought together on a spot

plate must always be mixed thoroughly: a glass stirrer (Fig. II, 5, 4) or a platinum wire may be employed.

Traces of turbidity and of colour are also readily distinguished in micro test-tubes ( $50 \times 8$  mm.) or in micro centrifuge tubes. As a general rule, these vessels are employed in testing dilute solutions so as to obtain a sufficient depth of colour. The liquid in a micro centrifuge tube or in a test-tube may be warmed in a special stand immersed in a water bath (compare Figs. II, 3, 12-13) or in the apparatus depicted in Fig. II, 6, 4. The latter is constructed of thin aluminium or nickel wire; the tubes will slip through the openings and rest on their collars. The wire holder is arranged to fit over a small beaker, which can be filled with water at the appropriate temperature.

For heating to higher temperatures ( $>100^\circ$ ) micro porcelain crucibles may be employed: they are immersed in an air bath (Fig. II, 5, 5) and the latter heated by a micro burner, or they can be heated directly on an asbestos mat. Small silica watch glasses also find application for evaporations.

It must be emphasised that all glass and porcelain apparatus, including spot plates and crucibles, must be kept scrupulously clean. It is a good plan to wash all apparatus (particularly spot plates) immediately after use. Glassware and porcelain crucibles are best cleaned by immersion in a chromic acid-sulphuric acid mixture or in a mixture of concentrated sulphuric acid and hydrogen peroxide, followed by washing with a liberal quantity of distilled water, and drying. The use of chromic acid mixture is not recommended for spot plates.

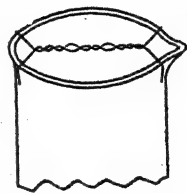


Fig. II, 6, 4

The great merit of glass and porcelain apparatus is that they can be employed with any strength of acid and base: they are also preferred when weakly coloured compounds (especially yellow) are produced or when the test depends upon slight colour differences. Filter paper, however, cannot be used with strongly acidic solutions for the latter cause it to tear, whilst strongly basic solutions produce a swelling of the paper. Nevertheless, for many purposes and especially for those dependent upon the application of capillary phenomena, spot reactions carried out on filter paper possess advantages over those in glass or porcelain: the tests generally have greater sensitivity and a permanent (or semi-permanent) record of the experiment is obtained.

**Spot reactions upon filter paper** are usually performed with Whatman drop reaction paper No. 120, but in some cases Whatman No. 3MM is utilised: the Schleicher and Schuell (U.S.A.) equivalents are Nos. 601 and 598. These papers possess the desirable property of rapidly absorbing the drops without too much spreading, as is the case with thinner papers. Although impurities have been

reduced to minimum values, they may contain traces of iron and phosphate: spot reactions for these are better made with quantitative filter paper (Whatman No. 42 or, preferably, the hardened variety No. 542). The paper should be cut into strips  $6 \times 2$  cm. or  $2 \times 2$  cm., and stored in petri dishes or in vessels with tightly-fitting stoppers.

Spot test papers are marketed in which the spot reaction is confined to a uniform area of fixed dimensions, produced by surrounding the area by a chemically inert, water-repelling barrier. These papers were developed by H. Yagoda and may be employed for semi-quantitative work. The Schleicher and Schuell (U.S.A.) No. 211Y "confined spot test" paper is intended for use with single drops of solution, and No. 597Y for somewhat larger volumes. They are often referred to as Yagoda test papers.

Spot reactions on paper do not always involve interaction between a drop of the test solution and one of the reagent. Sometimes the paper is impregnated with the reagent and the **dry impregnated reagent paper** is spotted with a drop of the solution. Special care must be taken in the choice of the impregnating reagent. Organic reagents, that are only slightly soluble in water but dissolve readily in alcohol or other organic solvents, find extensive application. Water-soluble salts of the alkali metals are frequently not very stable in paper. This difficulty can often be surmounted by the use of sparingly soluble salts of other metals. In this way the concentration of the reactive ion can be regulated automatically by the proper selection of the impregnating salt, and the specificity of the test can be greatly improved by thus restricting the number of possible reactions. Thus potassium xanthate (see under Molybdenum, Section IX, 4, reaction 3) has little value as an impregnating agent since it decomposes rapidly and is useless after a few days. When, however, cadmium xanthate is used, a paper is obtained which gives sensitive reactions only with copper and molybdenum and it will keep for months. Similarly the colourless zinc ferrocyanide offers parallel advantages as a source of ferrocyanide ions: it provides a highly sensitive test for ferric ions. A further example is paper impregnated with zinc, cadmium or antimony sulphides: such papers are stable, each with its maximum sulphide ion concentration (controlled by its solubility product) and hence only those metallic sulphides are precipitated whose solubility products are sufficiently low. Antimonious sulphide paper precipitates only Ag, Cu and Hg in the presence of Pb, Cd, Sn, Fe, Ni, Co and Zn. It might be expected that the use of "insoluble" reagents would decrease the reaction rate. This retardation is not significant when paper is the medium because of the fine state of division and the great surface available. Reduction in sensitivity becomes appreciable only when the solubility products of the reagent and the reaction product approach the same order of magnitude. This is naturally avoided in the selection of the reagents.



**Filter paper may be impregnated** with reagents by the following methods:

(i) For reagents that are soluble in water or in organic solvents, strips of filter paper are bathed in the solutions contained in beakers or in dishes. Care must be taken that the strips do not stick to the sides of the vessel or to one another, as this will prevent a uniform impregnation. The immersion should last about 20 minutes and the solution stirred frequently or the vessel gently rotated to produce a swirling of the solution. The strips are removed from the bath, allowed to drain, pinned to a string (stretched horizontally) and allowed to dry in the air. Uniform drying is of great importance.

Alternatively, the reagent may be sprayed on to the filter paper.

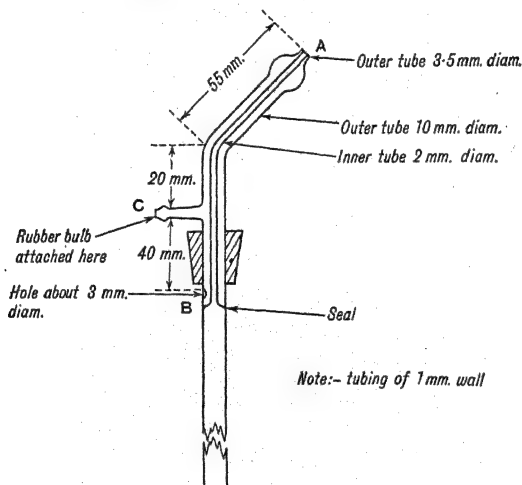


Fig. II, 6, 5

The all-glass spray shown in Fig. II, 6, 5 (not drawn to scale) gives excellent results. A rubber bulb is attached at C; the cork is fitted into a boiling tube or small flask charged with the impregnating solution. The paper is sprayed first on one side and then on the other.

(ii) For reagents that are precipitated on the paper, the strips are soaked rapidly and uniformly with the solution of one of the reactants, dried and then immersed similarly in a solution of the precipitant. The excess reagents are then removed by washing, and the strips dried. The best conditions (concentration of solutions, order in which applied, etc.) must be determined by experiment. In preparing highly impregnated papers, the precipitation should never be made with concentrated solutions as this may lead to an inhomogeneous precipitation and the reagent will tend to fall

off the paper after it is washed and dried. It is essential to carry out the soaking and precipitation separately with dilute solutions and to dry the paper between the individual precipitations. Sometimes it is preferable to use a reagent in the gaseous form, *e.g.* hydrogen sulphide for sulphides and ammonia for hydroxides; there is then no danger of washing away the precipitate.

The reactions are carried out by adding a drop of the test solution from a capillary pipette, etc., to the centre of the horizontal reagent paper resting across a porcelain crucible or similar vessel: an unhindered capillary spreading follows and a circular spot results. With an impregnated reagent paper, the resulting change in colour may occur almost at once, or it may develop after the application of a further reagent. It is usually best not to place a drop of the test solution on the paper but to allow it to run slowly from a capillary tip (0.2–1 mm. diameter) by touching the tip on the paper. The test drop then enters over a minute area, precipitation



Fig. II, 6, 6

Actual size

or adsorption of the reaction product occurs in the immediate surrounding region, where it remains fixed in the fibres whilst the clear liquid spreads radially outwards by capillarity. A concentration of the coloured product, which would otherwise be spread over the whole area originally wetted by the test drop, is obtained, thus rendering minute quantities distinctly visible. A greater sensitivity is thus obtained than by adding a free drop of the test solution. Contact with the fingers should be avoided in manipulation with drop-reaction papers: a corner of the strip should be held with a pair of clean forceps.

The problem of **separating solid and liquid phases** either before or after taking a sample drop or two of the test solution frequently arises in spot test analysis.

When there is a comparatively large volume of liquid and the solid matter is required, centrifugation in a micro centrifuge tube (Fig. II, 5, 1) may be employed. Alternatively, a micro sintered glass filter tube (Fig. II, 6, 6), placed in a test-tube of suitable size, may be subjected to centrifugation: this device simplifies the washing of a precipitate. If the solid is not required, the liquid may be collected in a capillary pipette by sucking through a small pad of purified cotton wool placed in the capillary end; upon removing the cotton wool and wiping the pipette, the liquid may be delivered clear and free from suspended matter.

A useful **filter pipette** is shown in Fig. II, 6, 7. It is constructed of tubing of 6 mm. in diameter. A rubber bulb is attached to the short arm A; the arm B is ground flat, whilst the arm C is drawn out to a fine capillary; a short piece of rubber tubing is fitted over the top of B. For filtering, a disc of filter paper of the same diameter as the outside diameter of the tube (cut out from filter paper by means of a sharp cork borer or by a hand punch) is placed on

the flat ground surface of B, the tube F placed upon it and then held in position by sliding the rubber tubing just far enough over

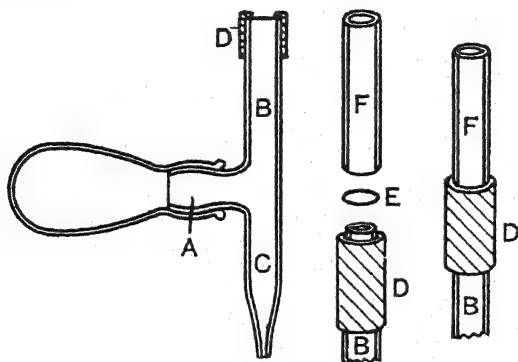


Fig. II, 6, 7

the paper to hold it when the tube F is removed. The filter pipette may be used either by placing a drop of the solution on the filter disc or by immersing the tube end B into the crucible, test-tube or receptacle containing the solution to be filtered. The bulb is squeezed by the thumb and middle finger, and the dropper point closed with the fore-finger thus allowing the solution to be drawn through the paper when the bulb is released. To release the drops of filtered liquid thus obtained, the filter pipette is inverted over the spot plate, etc., in an inclined position with the bulb uppermost. Manipulation of the bulb again forces the liquid in the tip on to the spot plate, etc. The precipitate on the paper can be withdrawn for any further treatment by simply sliding the rubber tubing D down over the arm B.

Another method involves the use of an **Emich filter stick** fitted through a rubber stopper into a thick-walled suction tube; the filtrate is collected in a micro test-tube (Fig. II, 6, 8). The filter stick has a small pad of purified asbestos above the constriction.

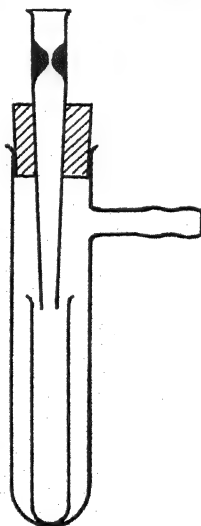


Fig. II, 6, 8

Two-thirds actual size

The apparatus illustrated in Fig. II, 6, 9 may be employed when the filter paper (or drop reaction paper) must be **heated in steam**; the filter paper is placed on the side arm support. By charging the flask with hydrogen sulphide solution, ammonia solution, chlorine or bromine water, the apparatus can be used for treating the filter paper with the respective gases or vapours.

**Fusion** and solution of a melt may be conducted either in a platinum wire loop or in a platinum spoon (0.5–1 ml. capacity) attached to a heavy platinum wire and fused into a glass holder.

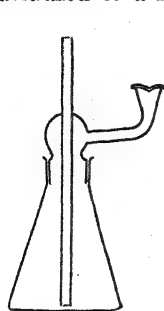


Fig. II, 6, 9

One-quarter  
actual size

**Gas reactions** may be performed in specially devised apparatus. Thus in testing for carbonates, sulphides, etc., it is required to absorb the gas liberated in a drop of water or reagent solution. The apparatus is shown in Fig. II, 6, 10, and consists of a micro test-tube of about 1 ml. capacity, which can be closed with a small ground glass stopper fused to a glass knob. The reagent and test solution or test solid are placed in the bottom of the tube, and a drop of the reagent for the gas is suspended on the knob of the stopper. The gas is evolved in the tube, if necessary, by gentle warming, and is absorbed by the reagent on the knob. Since the apparatus is closed, no gas can escape, and if sufficient time is allowed it is absorbed quantitatively by the

reagent. A drop of water may replace the reagent on the stopper; the gas is dissolved, the drop may be washed on to a spot plate or

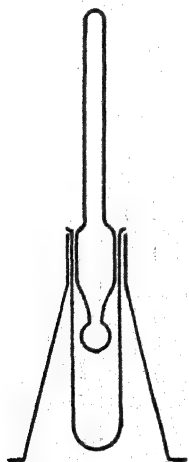


Fig. II, 6, 10

Actual size

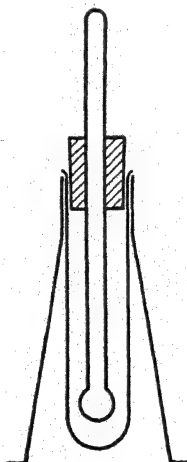


Fig. II, 6, 11

Actual size

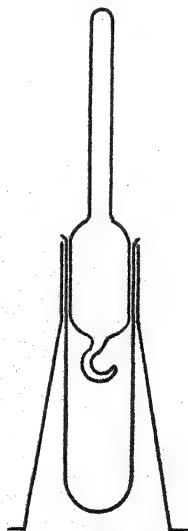


Fig. II, 6, 12

Actual size

into a micro crucible and treated with the reagent. The apparatus, shown in Fig. II, 6, 11, which is closed by a rubber stopper, is sometimes preferable, particularly when minute quantities of gas are

concerned; the glass tube, blown into a small bulb at the lower end, may be raised or lowered at will, whilst the change of colour and reaction products may be rendered more easily visible by filling the bulb with gypsum or magnesia powder. In some reactions, *e.g.* in testing for ammonia, it may be desirable to suspend a small strip of reagent paper from a glass hook fused to the stopper as in Fig. II, 6, 12. When a particular gas has to be identified in the presence of other gases, the apparatus shown in Fig. II, 6, 13 should be used; here the stopper for the micro test-tube consists of a small glass funnel on top of which the impregnated filter paper is laid in order to absorb the gas. The impregnated filter paper permits the passage of the indifferent gases and only retains the gas to be tested by the formation of a non-volatile compound that can be identified by means of a spot test. Another useful apparatus is shown in

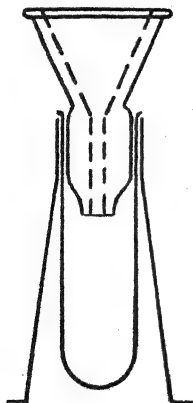


Fig. II, 6, 13  
Actual size

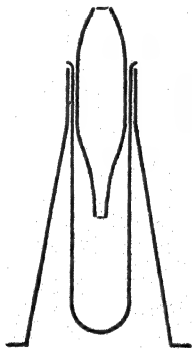


Fig. II, 6, 14  
Actual size

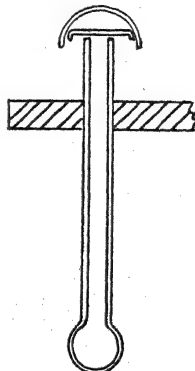


Fig. II, 6, 15  
Actual size

Fig. II, 6, 14; it consists of a micro test-tube into which is placed a loosely-fitting glass tube narrowed at both ends. The lower capillary end is filled to a height of about 1 mm. with a suitable reagent solution; if the gas liberated forms a coloured compound with the reagent, it can easily be seen in the capillary.

Where **high temperatures or glowing** are necessary for the evolution of the gas, a simple hard glass tube supported in a circular hole in an asbestos or "uralite" plate (Fig. II, 6, 15) may be used. The open end of the tube should be covered by a small piece of reagent paper and kept in position by means of a glass cap.

**Micro distillation** is sometimes required, *e.g.* in the chromyl chloride test for a chloride (see Section IV, 14, reaction 5). The apparatus depicted in Fig. II, 6, 16 is suitable for the distillation of very small quantities of a mixture. A micro crucible or a micro centrifuge tube may be employed as a receiver.

In Chapters III, IV and IX the experimental details are given for the detection of a number of elements or radicals by spot tests. These tests are set out in small (9 point) type as distinct from the other reactions which are in larger type: they can thus be readily distinguished and this is further facilitated by the use of a dagger (†) preceding the small type. The sensitivities given are, as a general

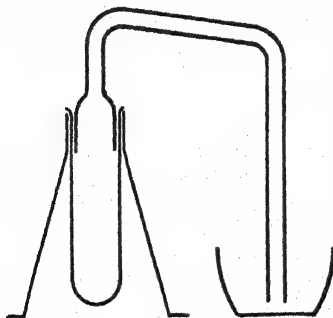


Fig. II, 6, 16

Actual size

rule, for a solution containing only the ion in question. It must be remembered that this is the most favourable case, and that in actual practice the presence of other ions usually necessitates a modification of the procedure, which is frequently indicated, and which, more often than not, involves a loss of sensitivity. Almost without exception each test is subject to interference from the presence of other ions, and the possibility of these interferences occurring must be taken into consideration when a test is applied. Furthermore,

the sensitivities when determined upon drop-reaction paper will depend upon the type of paper used. The figures given in the text have been obtained largely with the Schleicher and Schuell spot paper: substantially similar results are given by the equivalent Whatman papers. For purposes of reference the following equivalent papers are tabulated:

<i>Schleicher and Schuell paper</i>	<i>Whatman paper</i>
No. 601, "spot paper."	Drop-reaction paper, No. 120, double thickness.
No. 598.	No. 3 MM., 1st quality.
No. 589.	No. 42 or No. 542.

It is important to draw attention to the difference between the terms "specific" and "selective" when used in connexion with reagents or reactions. Reactions (and reagents), which under the experimental conditions employed are indicative of one substance (or ion) only are designated as **specific**, whilst those reactions (and reagents) which are characteristic of a comparatively small number of substances are classified as **selective**. Hence we may describe reactions (or reagents) as having varying degrees of selectivity; however, a reaction (or reagent) can be only specific or not specific.

## CHAPTER III

### REACTIONS OF THE METAL IONS OR CATIONS

**III, 1. The Analytical Classification of the Metals.**—The common metallic ions may be divided, for purposes of qualitative analysis, into a number of groups which are distinguished by the fact that the metals of any group are precipitated by a particular group reagent. Thus by the addition of a slight

<i>Group</i>	<i>Group reagent</i>	<i>Ions</i>	<i>Formula of precipitate</i>	<i>Distinguishing features</i>
<b>I</b> ( <i>Silver group</i> )	Dilute HCl	$\text{Ag}^+$ , $\text{Pb}^{++}$ , $\text{Hg}_2^{++}$	$\text{AgCl}$ , $\text{PbCl}_2$ , $\text{Hg}_2\text{Cl}_2$	Chlorides insoluble in cold dilute HCl.
<b>II</b> ( <i>Copper and arsenic groups</i> )	$\text{H}_2\text{S}$ in presence of dilute HCl	$\text{Hg}^{++}$ , $\text{Pb}^{++}$ , $\text{Bi}^{+++}$ , $\text{Cu}^{++}$ , $\text{Cd}^{++}$ , $\text{Sn}^{++}$ , $\text{As}^{+++}$ , $\text{Sb}^{+++}$ , $\text{Sn}^{++++}$	$\text{HgS}$ , $\text{PbS}$ , $\text{Bi}_2\text{S}_3$ , $\text{CuS}$ , $\text{CdS}$ , $\text{SnS}$ , $\text{As}_2\text{S}_3$ , $\text{Sb}_2\text{S}_3$ , $\text{SnS}_2$	Sulphides insoluble in dilute HCl (ca. 0.3N)
<b>IIIA</b> ( <i>Iron group</i> )	Aq. $\text{NH}_3$ in presence of $\text{NH}_4\text{Cl}$	$\text{Al}^{+++}$ , $\text{Cr}^{+++}$ , $\text{Fe}^{+++}$	$\text{Al}(\text{OH})_3$ , $\text{Cr}(\text{OH})_3$ , $\text{Fe}(\text{OH})_3$	Hydroxides pptd. by aq. $\text{NH}_3$ in presence of excess of $\text{NH}_4\text{Cl}$ .
<b>IIIB</b> ( <i>Zinc group</i> )	$\text{H}_2\text{S}$ in presence of aq. $\text{NH}_3$ and $\text{NH}_4\text{Cl}$	$\text{Ni}^{++}$ , $\text{Co}^{++}$ , $\text{Mn}^{++}$ , $\text{Zn}^{++}$	$\text{NiS}$ , $\text{CoS}$ , $\text{MnS}$ , $\text{ZnS}$	Sulphides pptd. by $\text{H}_2\text{S}$ in presence of aq. $\text{NH}_3$ and $\text{NH}_4\text{Cl}$ .
<b>IV</b> ( <i>Calcium group</i> )	$(\text{NH}_4)_2\text{CO}_3$ in presence of aq. $\text{NH}_3$ and $\text{NH}_4\text{Cl}$	$\text{Ba}^{++}$ , $\text{Sr}^{++}$ , $\text{Ca}^{++}$	$\text{BaCO}_3$ , $\text{SrCO}_3$ , $\text{CaCO}_3$	Carbonates pptd. by $(\text{NH}_4)_2\text{CO}_3$ in presence of $\text{NH}_4\text{Cl}$ .
<b>V</b> ( <i>Alkali group</i> )	No particular reagent	$\text{Mg}^{++}$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{NH}_4^+$	$\text{Mg}^{++}$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{NH}_4^+$ , in solution	Ions not pptd. in previous groups.

excess of dilute hydrochloric acid to a solution containing all the common metallic ions, a precipitate is obtained consisting of the chlorides of silver, lead and mercurous mercury. These metal ions are therefore classed together in Group I; their chlorides are insoluble in cold, dilute hydrochloric acid (ca. 0.3*N*). Similarly by the use of the appropriate group reagents, the remaining metallic ions are separated into different groups. In general, it may be stated that the classification is based upon the varying solubilities of the chlorides, sulphides, hydroxides and carbonates.

The various groups are summarised in the table on the previous page.

Ammonium is detected in the original substance by boiling a small portion with sodium hydroxide solution before carrying out the separation of the metal ions into groups.

It is assumed in the above table that the group reagents are added systematically to the solutions from which the ions of the earlier groups have been removed. Thus dilute hydrochloric acid is added to the original solution, hydrogen sulphide is passed into the filtrate from Group I, ammonium chloride and aqueous ammonia solutions are added to the filtrate from Group II, and so on.

A knowledge of the reaction of the various ions is necessary in order to understand the processes involved in the separation of the members of the various groups and generally to appreciate the subject of qualitative analysis. A systematic account of the more common metal ions arranged in order of the groups is given in the following pages.

The reactions will be expressed largely as molecular equations. Many of these should, of course, be written as ionic equations: the student is therefore recommended to rewrite, where applicable, the molecular equations in their ionic forms, and this should be regarded as an essential part of the study of the reactions of the various cations and anions. The so-called ammonium hydroxide reagent is a solution of ammonia gas in water and it is doubtful whether the undissociated base  $\text{NH}_4\text{OH}$  has any actual existence (see Sections I, 5 and I, 42): the reagent will be termed **ammonia solution** in the text. It will be appreciated that the basic character of ammonia solution ( $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$ ) is readily understood on the Lowry-Brønsted theory (see Section I, 42). For the sake of simplicity, the unhydrated hydrogen ion  $\text{H}^+$  will be employed in equations for the hydroxonium ion  $\text{H}_3\text{O}^+$ ; in aqueous solution it is, of course, the hydrated proton and not



the free proton that is present (see Section I, 5). Mention should also be made of the fact that a solution of hydrogen sulphide in aqueous ammonia contains mainly ammonium hydrosulphide  $\text{NH}_4\text{HS}$ ; the existence of the normal sulphide  $(\text{NH}_4)_2\text{S}$  in aqueous solution is very doubtful and, in any case, would be almost completely hydrolysed (compare *Example 22* in Section I, 40).

When carrying out the various reactions of cations and anions, the student may adopt either the macro or semimicro technique. For the former test-tubes ( $150 \times 19$  mm.), beakers, conical flasks (50 ml.), etc., are employed: the student should always aim to keep the volumes and quantities of reagents as small as possible. The advantages of the semimicro technique, especially from the viewpoint of economy of chemicals and apparatus (see paragraphs before Section II, 1), are so great that it must be strongly recommended to all. Reactions are performed in 4 ml. test-tubes ( $75 \times 10$  mm.) or 3 ml. centrifuge tubes, the precipitates are separated from the supernatant liquids by centrifugation, evaporations are conducted in either 5–8 ml. porcelain crucibles or in 20 ml. boiling tubes, etc. (see Section II, 3). Alternative tables of separation for macro and semimicro work will be provided.

As an illustration of the economy of chemicals and of time on the semimicro scale, details will be given as to how reaction 1 for lead and silver ions (Sections III, 2 and III, 4) may be carried out. To 2 drops of the test solution of  $\text{Pb}^{++}$  contained in a 3 ml. centrifuge tube add 2 drops of dilute hydrochloric acid. Observe the nature, size and colour of the precipitate. Centrifuge the mixture: remember to balance the test-tube with another similar tube containing the same volume of water. Remove the supernatant liquid, called the *centrifugate*, by means of a capillary dropper to another centrifuge tube, test it with another drop of dilute hydrochloric acid to ensure complete precipitation, and then reject the solution. Treat the precipitate, termed the *residue*, with 2 drops of distilled water, stir and centrifuge. Remove the liquid, called the *washings*, and reject it. Add 5 drops of distilled water to the residue, stir and place the tube in a boiling water bath. Stir while heating: note that the precipitate dissolves completely. To the solution add 1 drop of dilute acetic acid and 1 drop of potassium chromate solution. A yellow precipitate of lead chromate separates.

To 2 drops of the test solution of  $\text{Ag}^+$  contained in a 3 ml. centrifuge tube add 2 drops of dilute hydrochloric acid. Observe the nature, colour and size of the precipitate. Centrifuge and discard the centrifugate. Wash the precipitate by adding 2 drops of distilled water, stir and centrifuge: discard the washings. Treat

the residue of silver chloride with 5 drops of dilute aqueous ammonia and stir until complete solution takes place. Now add dilute nitric acid, drop by drop, stirring the mixture after each addition, until acid (test by removing a drop of the stirred mixture on to blue litmus paper). Observe the formation of a white precipitate of silver chloride.

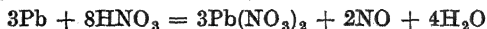
## THE SILVER GROUP (GROUP I)

### LEAD, MERCURY (OUS) AND SILVER

The compounds of these metals are characterised by their precipitation as chlorides by dilute hydrochloric acid or by a soluble chloride. Lead chloride is slightly soluble in water and hence is not completely precipitated as chloride in this group; it is therefore also found in Group II, where it is precipitated as the highly insoluble sulphide.

#### LEAD, Pb

Lead is a bluish-grey metal with a density of 11.48. It is readily dissolved by dilute nitric acid:

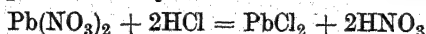


With concentrated nitric acid, a protective film of lead nitrate, which is insoluble in this acid, prevents complete solution. Dilute hydrochloric acid and dilute sulphuric acid have little action owing to the formation of protective films of lead chloride and sulphate respectively.

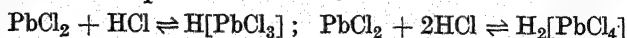
### III, 2. REACTIONS OF THE LEAD ION, $\text{Pb}^{++}$

Use a solution of lead nitrate,  $\text{Pb}(\text{NO}_3)_2$ , or of lead acetate,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$  (abbreviated to  $\text{Pb}\bar{\text{A}}_2 \cdot 3\text{H}_2\text{O}$ ), acidified with a little acetic acid  $\text{H} \cdot \text{C}_2\text{H}_3\text{O}_2$  (or  $\text{H}\bar{\text{A}}$ ).\*

**1. Dilute Hydrochloric Acid:** white precipitate of lead chloride  $\text{PbCl}_2$ , formed only in cold and not too dilute solution:

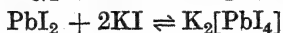
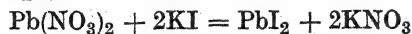


The precipitate is soluble in hot water (33.4 g. and 9.9 g. per litre at  $100^\circ$  and  $20^\circ$  respectively), but separates out again in needles when the solution is cooled. It is also soluble in concentrated hydrochloric acid and in concentrated alkali chloride solutions owing to the formation of complex compounds (compare Section I, 19); these are decomposed on dilution with water with the separation of lead chloride:

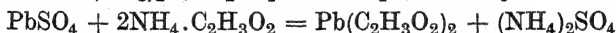
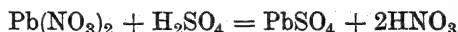


\* It is recommended that the test solutions employed in the study of the reactions of the cations and anions described in Chapters III and IV be prepared as detailed in the Appendix (Section A, 3). These contain 10 milligrams of the cation or anion per ml.

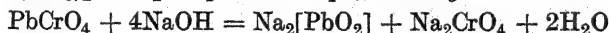
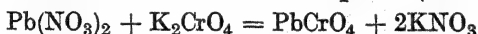
**2. Potassium Iodide Solution:** yellow precipitate of lead iodide  $\text{PbI}_2$ , moderately soluble in boiling water to yield a colourless solution from which it separates on cooling in golden yellow plates. It is also soluble in excess of potassium iodide solution forming a complex salt, which is decomposed on dilution with deposition of lead iodide.



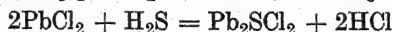
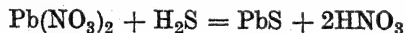
**3. Dilute Sulphuric Acid:** white precipitate of lead sulphate  $\text{PbSO}_4$ , insoluble in excess, but soluble in a concentrated solution of ammonium acetate (due to the formation of lead acetate, which is little ionised in the presence of excess of acetate ions; see Common Ion Effect, Section I, 14) or in an ammoniacal solution of ammonium tartrate.



**4. Potassium Chromate Solution:** yellow precipitate of lead chromate  $\text{PbCrO}_4$ , insoluble in acetic acid and in ammonia solution, but soluble in alkali hydroxides and in nitric acid. Lead chromate is quantitatively precipitated from an ammonium acetate solution of lead sulphate (reaction 3).



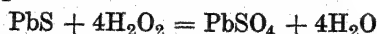
**5. Hydrogen Sulphide:** black precipitate of lead sulphide  $\text{PbS}$ . The precipitate is often red in the presence of hydrochloric acid; this is due to the initial formation of lead sulphochloride  $\text{Pb}_2\text{SCl}_2$ , which is decomposed on dilution and by passage of excess of hydrogen sulphide forming black lead sulphide.



The precipitate of lead sulphide is very slightly soluble in solutions of alkali polysulphides, insoluble in alkali monosulphides, but soluble in hot dilute nitric acid:



It is converted into white lead sulphate  $\text{PbSO}_4$  on treatment with hydrogen peroxide:

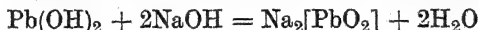
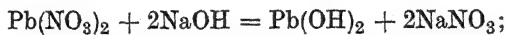


The great insolubility of lead sulphide in water ( $4.9 \times 10^{-11}$  g. per litre) explains why hydrogen sulphide is such a sensitive reagent for the detection

of lead, and why it can be detected in the filtrate from the separation of the sparingly soluble lead chloride in dilute hydrochloric acid.

**Note.**—*Hydrogen sulphide is a highly poisonous gas, and all operations with the gas must be conducted in the fume chamber. Every precaution must be observed to prevent the escape of hydrogen sulphide into the air of the laboratory.*

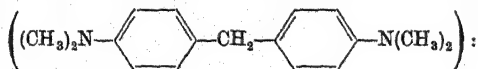
**6. Sodium Hydroxide Solution:** white precipitate of lead hydroxide  $\text{Pb}(\text{OH})_2$ , soluble in excess of the reagent to form sodium plumbite:



Hydrogen peroxide or a solution of a persulphate precipitates brown lead dioxide  $\text{PbO}_2$  from a solution of sodium plumbite.

Ammonia solution yields the white lead hydroxide, insoluble in excess of precipitant.

†7. **Tetramethyldiamino-diphenylmethane (or "Tetra-base") Reagent**



a blue oxidation product {hydrol:  $-\text{CH}_2 \rightarrow -\text{CH}(\text{OH})$ } is formed under the conditions given below.

Place 1 ml. of the test solution in a 5 ml. centrifuge tube, add 1 ml. of 2N potassium hydroxide and 0.5–1 ml. of 3 per cent hydrogen peroxide solution. Allow to stand for 5 minutes. Separate the precipitated lead plumbate by centrifugation, and wash once with cold water. Add 2 ml. of the reagent, shake and centrifuge. The supernatant liquid is coloured blue.

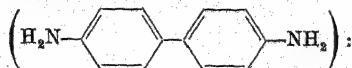


The ions of Bi, Ce, Mn, Tl, Co and Ni give a similar reaction: Fe and large quantities of Cu interfere.

Concentration limit: 1 in 10,000.

The reagent is prepared by dissolving 0.5 g. of the "tetra-base" in a mixture of 20 ml. of glacial acetic acid and 80 ml. of 96 per cent ethyl alcohol.

†8. **Benzidine Reagent**



the so-called "benzidine blue" is produced upon oxidation with lead dioxide. The ions of Bi, Ce, Mn, Co, Ni, Ag and Tl give a similar reaction, but by performing the test in an alkaline extract (*i.e.* with a plumbite solution), only Tl interferes. Oxidation is conveniently

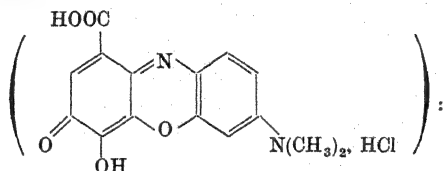
carried out by sodium hypobromite; the excess of the latter is destroyed by ammonia:  $2\text{NH}_3 + 3\text{NaOBr} = \text{N}_2 + 3\text{NaBr} + 3\text{H}_2\text{O}$ .

Place a drop of the test solution upon drop-reaction paper, and treat successively with 2 drops of 3*N* sodium hydroxide and 1 drop of saturated bromine water. Add 2 drops of 1 : 1-ammonia solution; remove the excess of ammonia by waving the paper over a small flame. Add 2 drops of the reagent; a blue colour develops.

Sensitivity: 1  $\mu\text{g}$ . Pb. Concentration limit: 1 in 50,000.

The reagent is a 0.05 per cent solution of benzidine in 10 per cent acetic acid.

#### †9. Gallocyanine Reagent



deep violet precipitate of unknown composition. The test is applicable to finely-divided lead sulphate precipitated on filter paper.

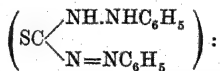
Place a drop of the test solution upon drop-reaction paper, followed by a drop each of 1 per cent aqueous pyridine and the gallocyanine reagent (blue). Remove the excess of the reagent by placing several filter papers beneath the drop-reaction paper and adding drops of the pyridine solution to the spot until the wash liquid percolating through is colourless; move the filter papers to a fresh position after each addition of pyridine. A deep violet spot is produced.

Sensitivity: 1–6  $\mu\text{g}$ . Pb. Concentration limit: 1 in 50,000.

In the presence of silver, bismuth, cadmium or copper, proceed as follows. Transfer a drop of the test solution to a drop-reaction paper and add a drop of 2*N*-sulphuric acid to fix the lead as lead sulphate. Remove the soluble sulphates of the other metals by washing with about 3 drops of 2*N*-sulphuric acid, followed by a little rectified spirit. Dry the paper on a water bath, and then apply the test as detailed above.

The reagent consists of a 1 per cent aqueous solution of gallocyanine.

#### †10. Diphenylthiocarbazon (or Dithizone) Reagent



brick-red complex salt in neutral, ammoniacal, alkaline or alkali-cyanide solution.

Place 1 ml. of the neutral or faintly alkaline solution in a micro test-tube, introduce a few small crystals of potassium cyanide, and then 2 drops of the reagent. Shake for 30 seconds. The green colour of the reagent changes into red.

Sensitivity: 0.1  $\mu\text{g}$ . Pb (in neutral solution). Concentration limit: 1 in 1,250,000.

Heavy metals (Ag, Hg, Cu, Cd, Sb, Ni, Zn, etc.) interfere, but this effect may be eliminated by conducting the reaction in the presence of

much alkali cyanide: excess of KOH solution is also required for Zn. The reaction is extremely sensitive, but it is not very selective.

The reagent is prepared by dissolving 2-5 mg. of dithizone in 100 ml. of carbon tetrachloride or chloroform. It does not keep well.

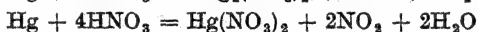
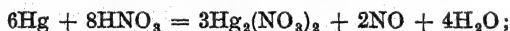
### Dry Tests

(i) *Blowpipe test*.—When a lead salt is heated with alkali carbonate upon charcoal, a malleable bead of lead (which is soft and will mark paper), surrounded with a yellow incrustation of lead monoxide, is obtained.

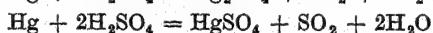
(ii) *Flame test*.—Pale blue (inconclusive).

### MERCURY Hg

Mercury is a silvery-white, liquid metal at the ordinary temperature and has a density ( $d_4^{20}$ ) of 13.595. It is unaffected by treatment with dilute hydrochloric or dilute sulphuric acid, but reacts readily with nitric acid. Cold dilute nitric acid and excess of mercury yield mercurous nitrate, whilst with excess of the hot concentrated acid mercuric nitrate is produced:



With hot concentrated sulphuric acid, mercurous or mercuric sulphate is formed according as the metal or the acid is present in excess;

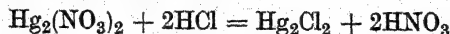


Mercury forms two series of salts: the mercurous compounds, corresponding to mercurous oxide  $\text{Hg}_2\text{O}$  and containing the bivalent mercurous group  $\text{Hg}_2^{++}$  ( $-\text{Hg}-\text{Hg}-$ ), and the mercuric compounds, corresponding to mercuric oxide and containing the bivalent ion  $\text{Hg}^{++}$ .

### III, 3. REACTIONS OF THE MERCUROUS ION, $\text{Hg}_2^{++}$

Use a solution of mercurous nitrate,  $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ .\*

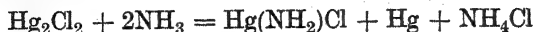
1. **Dilute Hydrochloric Acid**: white precipitate of mercurous chloride (calomel)  $\text{Hg}_2\text{Cl}_2$ , insoluble in hot water and in cold dilute acids, but soluble in aqua regia, whereby it is converted into mercuric chloride.



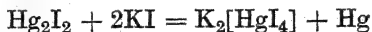
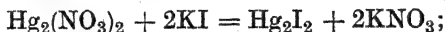
The precipitate becomes black when ammonia solution is poured over it, due to the production of amino-mercuric chloride ("infusible white precipitate") and finely divided

\* Use sufficient cold, dilute nitric acid to produce a clear solution.

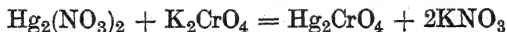
mercury (black); this black mixture is soluble in aqua regia with the formation of mercuric chloride:



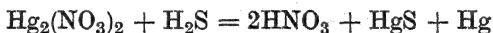
**2. Potassium Iodide Solution:** yellowish-green precipitate of mercurous iodide  $\text{Hg}_2\text{I}_2$ , which yields soluble potassium mercuri-iodide  $\text{K}_2[\text{HgI}_4]$  and black finely divided mercury with excess of the reagent.



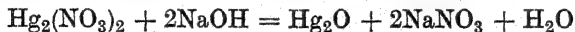
**3. Potassium Chromate Solution:** brown amorphous precipitate of mercurous chromate  $\text{Hg}_2\text{CrO}_4$  in the cold, which is converted into a red crystalline form on boiling.



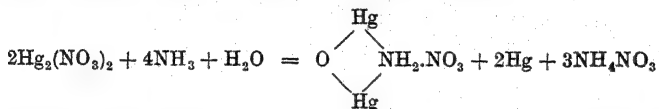
**4. Hydrogen Sulphide:** immediate black precipitate of mercuric sulphide  $\text{HgS}$  and mercury (difference from mercuric salts).



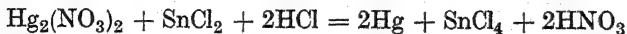
**5. Sodium Hydroxide Solution:** black precipitate of mercurous oxide  $\text{Hg}_2\text{O}$ , insoluble in excess of the precipitant.



**6. Ammonia Solution:** black precipitate, consisting of a mercuric amino salt and finely divided mercury.



**7. Stannous Chloride Solution:** grey, finely-divided mercury is obtained with excess of the reagent.



**8. Potassium Nitrite Solution:** mercury separates as a dark grey (or black) precipitate (distinction from mercuric salts).

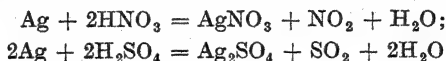
† The spot test technique is as follows. Place a drop of the faintly acid test solution upon drop-reaction paper and add a drop of concentrated potassium nitrite solution. A black (or dark grey) spot is produced. The test is highly selective. Coloured ions yield a brown coloration which may be washed away, leaving the black spot.

**Dry Tests**

See under Mercuric Ion, Section III, 6.

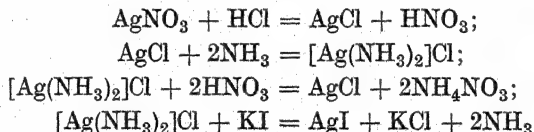
**SILVER Ag**

Silver is a white, malleable and ductile metal. It is insoluble in dilute hydrochloric and sulphuric acids, but dissolves readily in nitric acid (2:1) and in boiling concentrated sulphuric acid:

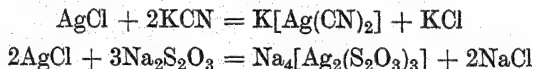
**III, 4. REACTIONS OF THE SILVER ION,  $\text{Ag}^+$** 

Use a solution of silver nitrate,  $\text{AgNO}_3$ .

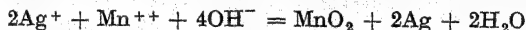
**1. Dilute Hydrochloric Acid:** white, curdy precipitate of silver chloride  $\text{AgCl}$ , which darkens on exposure to light. The precipitate is insoluble in water (solubility,  $1.5 \times 10^{-3}$  g. per litre) and in acids (including nitric acid), but is soluble in dilute ammonia solution owing to the formation of the complex ion,  $[\text{Ag}(\text{NH}_3)_2]^+$  (see Section I, 20). It is precipitated from the ammoniacal solution by the addition of dilute nitric acid; silver iodide is precipitated with potassium iodide solution.



Silver chloride is also soluble in potassium cyanide solution (*highly poisonous*) and in sodium thiosulphate solution:



† A useful spot test, which may be applied to a silver chloride precipitate, makes use of the reaction with manganous salts and alkali:



A stain of  $\text{AgCl}$  is thus coloured black. Mercurous and mercuric mercury, stannous tin and the noble metals interfere.

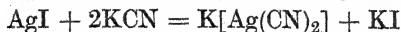
Place a drop of dilute  $\text{HCl}$ , followed by a drop of the test solution upon filter or drop reaction paper. Then add a drop of 2 per cent  $\text{MnSO}_4$  or  $\text{Mn}(\text{NO}_3)_2$  solution and a drop of 10 per cent  $\text{KOH}$  solution. A black stain is produced.

Sensitivity: 2  $\mu\text{g}$ . Ag. Concentration limit: 1 in 25,000.

**2. Potassium Iodide Solution:** yellow precipitate of silver iodide  $\text{AgI}$ , insoluble in concentrated ammonia solution, but



readily soluble in solutions of potassium cyanide and of sodium thiosulphate.



**3. Potassium Chromate Solution:** red precipitate of silver chromate  $\text{Ag}_2\text{CrO}_4$ , insoluble in dilute acetic acid, but soluble in dilute nitric acid and in ammonia solution.



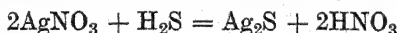
† The spot technique is as follows. Place a drop of the test solution on a watch glass or on a spot plate, add a drop of ammonium carbonate solution and stir (this renders any mercurous mercury or lead ions unreactive by precipitation as the highly insoluble carbonates). Remove one drop of the clear liquid and place it on drop-reaction paper together with a drop of the potassium chromate reagent. A red ring of silver chromate is obtained.

Sensitivity:  $2 \mu\text{g. Ag}$ . Concentration limit: 1 in 25,000.

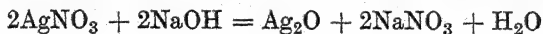
Alternatively, the reaction with the clear solution may be carried out on a spot plate, when red silver chromate is precipitated.

The reagent consists of a 1 per cent solution of potassium chromate in *N*-acetic acid.

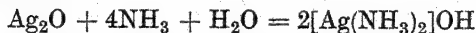
**4. Hydrogen Sulphide:** black precipitate of silver sulphide  $\text{Ag}_2\text{S}$ , insoluble in water (solubility,  $1 \times 10^{-11}$  g. per litre) and in ammonia solution, but soluble in hot dilute nitric acid.



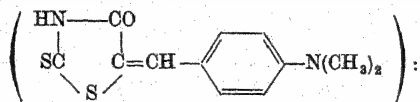
**5. Sodium Hydroxide Solution:** brown precipitate of silver oxide  $\text{Ag}_2\text{O}$ , insoluble in excess of the precipitant.



**6. Ammonia Solution:** white precipitate at first which quickly passes into brown silver oxide  $\text{Ag}_2\text{O}$ , soluble in excess of the precipitant.



†7. **para-Dimethylamino-benzylidene-rhodanine Reagent**



red-violet salt (Ag replaces H of HN group) in faintly acid solution. Mercury, cuprous copper, gold, platinum and palladium salts form similar compounds and therefore interfere.

Spot the test solution upon drop reaction paper, add 1 drop of  $N$  nitric acid, followed by a drop of the reagent. A red-violet precipitate or stain is formed according to the silver content of the test solution.

Alternatively, the test may be performed on a spot plate or in a semimicro test-tube; in the latter case the excess of the reagent is extracted with ether or amyl alcohol when violet specks of the silver complex will be visible under the yellow solvent layer.

Sensitivity:  $0.02 \mu\text{g. Ag.}$  (in  $0.2N$  nitric acid).

Concentration limit: 1 in 2,500,000.

If **mercury is present**, treat a drop of the test solution either on drop reaction paper or on a spot plate with a drop of 5 per cent potassium cyanide solution, followed by a drop of the reagent and a drop of  $2N$  nitric acid. The silver rhodanine complex is precipitated: the mercury is held in solution as undissociated mercuric cyanide.

If **gold, platinum and palladium are present** (copper must be absent since cuprous copper gives a violet precipitate in acid solution), mix on a spot plate 1 drop of the test solution with a drop of 10 per cent potassium cyanide solution and a drop of the reagent. Stir and acidify with  $3N$  nitric acid. A red colour is obtained in the presence of  $2.5 \mu\text{g.}$  of silver.

The reagent consists of a 0.03 per cent solution of *p*-dimethylamino-benzylidene-rhodanine in acetone or in alcohol.

To detect Ag in a mixture of  $\text{PbCl}_2$ ,  $\text{Hg}_2\text{Cl}_2$  and  $\text{AgCl}$  (Group I), the mixture is treated with 5 per cent potassium cyanide solution whereby  $\text{Hg}(\text{CN})_2 + \text{Hg}$  as well as  $\text{K}[\text{Ag}(\text{CN})_2]$  are formed: after filtration (or centrifugation), a little of the clear filtrate is treated on a spot plate with a drop of the reagent and 2 drops of  $2N$  nitric acid. A red coloration is formed in the presence of Ag in weakly acid solution.

## Dry Tests

*Blowpipe test.*—When a silver salt is heated with alkali carbonate on charcoal, a white malleable bead without an incrustation of the oxide results; this is readily soluble in nitric acid. The solution is immediately precipitated by dilute hydrochloric acid, but not by very dilute sulphuric acid (difference from lead).

### DETECTION AND SEPARATION OF METALS IN THE SILVER GROUP (GROUP I)

When the student has worked through the reactions of the metals in this group, he should attempt to identify the members of the group both singly and when present in a mixture in the solutions supplied to him by the teacher. With the aid of the following simplified table which is directly based upon the reactions already studied, this should prove a comparatively simple task. A more detailed table will be given when all the metals have been studied.

It is important that the student should acquire the habit of recording his results in tabular form.

## III, 5. Table I. Analysis of the Silver Group (Group I)

To the given solution (or to the solution of the substance in water), add dilute HCl in excess and filter. Discard the filtrate. (T)\* Wash the precipitate, which may contain  $\text{PbCl}_2$ ,  $\text{AgCl}$  and  $\text{Hg}_2\text{Cl}_2$ , with a little very dilute HCl (ca. 0.5N). Boil the precipitate with 5–10 ml. of water and filter hot.

**Residue.** May contain  $\text{Hg}_2\text{Cl}_2$  and  $\text{AgCl}$ . Wash the ppt. thoroughly with hot water until the extract gives no ppt. with  $\text{K}_2\text{CrO}_4$  solution, thus ensuring the complete removal of lead; reject the washings.

Pour 3–4 ml. of warm dilute  $\text{NH}_3$  solution over the ppt. on the filter.

**Residue.** Black.  
 $\text{Hg} + \text{Hg}(\text{NH}_2)\text{Cl}$ .  
Mercury  
present.

**Filtrate.** May contain  
 $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$ .  
Acidify with dilute  
 $\text{HNO}_3$ .  
White ppt. of  $\text{AgCl}$ .  
Silver present.

**Filtrate.** May contain  
 $\text{PbCl}_2$ . Divide into two  
parts:

(i) Add a little ammonium acetate solution followed by  $\text{K}_2\text{CrO}_4$  solution. Yellow ppt. of  $\text{PbCrO}_4$ .

(ii) Cool under tap. White crystalline ppt. of  $\text{PbCl}_2$ .

Lead present.

## III, 5. Table SMI. Analysis of the Silver Group (Group I)

To 1 ml. of the given solution in a 3 ml. centrifuge tube (or a 4 ml. test-tube), add 3–4 drops (1) of dilute HCl. Stir. Centrifuge. Remove the centrifugate with a dropper pipette to another tube, and test for completeness of precipitation with 1 drop of dilute HCl; if no ppt. forms, discard the solution. Wash the ppt. with 3 drops of dilute HCl, stir, and centrifuge. Remove and discard the washings. (T)\* The residue may contain  $\text{PbCl}_2$ ,  $\text{AgCl}$  and  $\text{Hg}_2\text{Cl}_2$ . Add 1 ml. of hot water to the ppt., place the tube in a boiling water bath for 1–2 minutes, and stir continuously. Centrifuge rapidly: separate the solution from the residue with a capillary pipette and transfer the clear solution to a centrifuge tube.

**Residue.** May contain  $\text{Hg}_2\text{Cl}_2$  and  $\text{AgCl}$ , and also some undissolved  $\text{PbCl}_2$ . To remove the latter, add 1.0 ml. of water, place the tube in a boiling water bath for 1 minute; centrifuge and reject the supernatant liquid. Treat the residue with 0.5 ml. of warm dilute aqueous  $\text{NH}_3$ , stir and centrifuge.

**Residue.** Black.  
 $\text{Hg} + \text{Hg}(\text{NH}_2)\text{Cl}$ .  
Mercury  
present.

**Centrifugate.** May contain  
 $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$ . Add dilute  
HCl or dilute  $\text{HNO}_3$  until  
acid (2).

White ppt. of  $\text{AgCl}$ .  
Silver present.

**Centrifugate.** May contain  
 $\text{PbCl}_2$ . Add 2 drops of ammonium  
acetate solution and  
1 drop of  $\text{K}_2\text{CrO}_4$   
solution.

Yellow ppt. of  
 $\text{PbCrO}_4$ .

Lead present.

\* The symbol (T) refers to the point at which the group separation is commenced in connexion with Table S (Section V, 8) and Table SM.S (Section VI, 9) respectively.

*Notes.*—(1) For the sake of uniformity throughout the text, a drop is intended to mean 0.05 ml.—the volume of the drop delivered by the common medicine dropper. If the instructions require the addition of 0.5 ml., this quantity can either be measured out in a small measuring cylinder or from a calibrated pipette, or 10 drops can be added directly from a reagent dropper provided, of course, that a drop from the latter does not differ appreciably from 0.05 ml. (see, however, Section II, 3, 3). It is recommended that all *droppers be calibrated* as follows. The dropper pipette is almost filled with water by alternately compressing and releasing the bulb whilst the capillary end is dipped into a small beaker containing distilled water. The dropper is held vertically over a clean, dry measuring cylinder, the bulb gently pressed and the number of drops counted until the meniscus reaches the 2 ml. mark. This process is repeated until two results are obtained which do not differ by more than two drops. A small label, stating the number of drops per ml., should be attached to the upper part of the dropper.

(2) As a rule, when a solution is to be rendered acidic or basic, an indicator test paper, such as litmus, should be used. The indicator test paper is placed on a watch glass. The solution is treated with acid or base dropwise and with stirring until the wet stirring rod when brought into contact with a dry spot on the indicator paper causes the appropriate change in colour. In the present instance, the addition of a micro drop of phenolphthalein to the liquid in the tube is satisfactory.

## THE COPPER AND ARSENIC GROUP (GROUP II)

### MERCURY (IC), LEAD, BISMUTH, COPPER, CADMIUM, ARSENIC, ANTIMONY AND TIN

The compounds of these elements are characterised by their precipitation as sulphides by hydrogen sulphide from 0.3N hydrochloric acid solution. The sulphides of arsenic, antimony and tin are soluble in both ammonium sulphide and in potassium hydroxide solution, whilst those of the remaining metals are practically insoluble. It is therefore usual to sub-divide this group into the copper group or Group IIA, comprising mercury, lead, bismuth, copper and cadmium, and the arsenic group or Group IIB, comprising arsenic, antimony and tin.

## THE COPPER GROUP (GROUP IIA)

### MERCURY, Hg

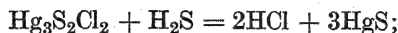
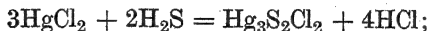
Mercury forms two series of compounds, the mercurous and mercuric, which may be regarded as derived respectively from the oxides  $\text{Hg}_2\text{O}$  and  $\text{HgO}$ . The reactions for the former have already been described (Section III, 3); those for the latter are detailed below.

It may be mentioned that mercuric chloride is only slightly dissociated in aqueous solution. Mercuric cyanide is soluble in water and practically undissociated; it will give a precipitate only with hydrogen sulphide.

### III, 6. REACTIONS OF THE MERCURIC ION, $\text{Hg}^{++}$

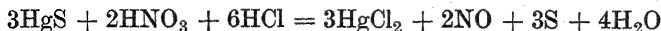
Use a solution of mercuric chloride,  $\text{HgCl}_2$  (*highly poisonous*).

**1. Hydrogen sulphide:** initially a white, then yellow, brown and finally a black precipitate of mercuric sulphide  $\text{HgS}$ . In all cases, excess of hydrogen sulphide gives the black mercuric sulphide. The white precipitate is the chlorosulphide  $\text{Hg}_3\text{S}_2\text{Cl}_2$  (or  $\text{HgCl}_2 \cdot 2\text{HgS}$ ), which is decomposed by hydrogen sulphide.

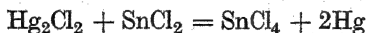
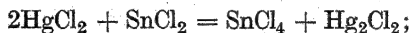


The net result is:  $\text{HgCl}_2 + \text{H}_2\text{S} = \text{HgS} + 2\text{HCl}$

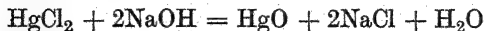
Mercuric sulphide is practically insoluble in water, hot dilute nitric acid, and in solutions of alkali hydroxides and of colourless ammonium sulphide. The precipitate is appreciably soluble in sodium sulphide solution and can be reprecipitated by adding ammonium chloride solution: it dissolves also in aqua regia and in a mixture of sodium hypochlorite solution and dilute hydrochloric acid.



**2. Stannous Chloride Solution:** a white precipitate of mercurous chloride  $\text{Hg}_2\text{Cl}_2$  is first obtained, which is reduced by excess of the reagent to grey-black metallic mercury.



**3. Sodium Hydroxide Solution:** initial reddish-brown precipitate of basic chloride, converted by excess of alkali into yellow mercuric oxide.



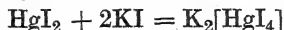
**4. Ammonia Solution:** white precipitate of amino mercuric chloride  $(\text{NH}_2)\text{HgCl}$ , known as "infusible white precipitate" for it volatilises without melting.



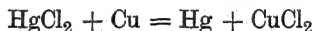
The precipitate is soluble in a large excess of aqueous ammonia and ammonium chloride.

**5. Potassium Iodide Solution:** red (initially yellow) precipitate of mercuric iodide  $\text{HgI}_2$ , soluble in excess of the

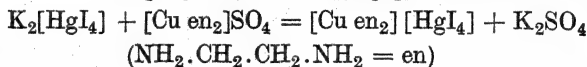
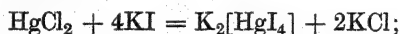
precipitant owing to the formation of the complex salt, potassium mercuri-iodide  $K_2[HgI_4]$  (compare Sections I, 19 and I, 20).



**6. Copper:** when a piece of bright copper foil, cleansed—if necessary—by rubbing it with emery paper or by dipping it into concentrated nitric acid, is immersed into the mercuric chloride solution, it becomes coated with a grey film of mercury, which acquires a silvery appearance on rubbing (see Electrode Potentials, Section I, 29).



**7. Ethylenediamine Reagent:** a dark blue-violet precipitate of the complex  $[Cu en_2] [HgI_4]$  is formed when a mercuric salt in neutral or faintly ammoniacal solution is treated with excess of 2 per cent potassium iodide solution, followed by the ethylenediamine reagent.



The reaction is a sensitive one, but cadmium ions, which form a similar complex  $[Cu en_2] [CdI_4]$ , interfere.

The reagent is prepared by treating a solution of cupric sulphate with an aqueous solution of ethylenediamine (5-6 times the theoretical quantity) until the dark blue-violet coloration, due to the  $[Cu en_2]^{++}$  ion, appears and does not increase in intensity upon further addition of the base. The presence of excess of the latter in the reagent has no harmful influence.

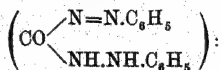
†8. **Stannous Chloride-Aniline Test.**—Mercuric salts are reduced to grey or black metallic mercury. The aniline adjusts the pH of the medium so that the similar reaction of  $Sb^{+++}$  does not occur. Large amounts of Ag interfere as do Au and Mo; Bi and Cu are without effect.

Treat a drop of the test solution upon drop reaction paper or upon a spot plate with a drop of the stannous chloride solution and a drop of aniline. A brown or black stain of Hg is produced.

Sensitivity: 1  $\mu g.$  Hg. Concentration limit: 1 in 50,000.

The reagent consists of a 5 per cent solution of stannous chloride in 10N hydrochloric acid.

#### †9. Diphenylcarbazone Reagent



blue to violet inner complex salt. The sensitivity of the test depends upon the pH of the solution, decreasing with increasing acidity. In 0.2N nitric acid, the test is highly selective provided chromates and molybdates (which give coloured compounds) are absent. Chromates may be reduced with sulphurous acid or with hydrogen peroxide to non-reacting chromic salts; molybdates may be rendered inactive by adding 5 per cent oxalic acid solution when a Mo-oxalic acid complex is produced.

Place a drop of the test solution and a drop of 0.2N nitric acid upon drop reaction paper, which has been moistened with the reagent. A violet or blue coloration appears.

Sensitivity: 1  $\mu$ g. Hg. Concentration limit: 1 in 50,000.

The reagent consists of a 1 per cent solution of diphenylcarbazone in 90–100 per cent ethyl alcohol.

†10. **Cobalt Acetate-Ammonium Thiocyanate Reagent.**—When a solution of a mercuric salt is treated with a concentrated solution of cobalt acetate and a little solid ammonium thiocyanate, a deep-blue crystalline precipitate of cobaltous mercuri-thiocyanate  $\text{Co}[\text{Hg}(\text{CNS})_4]$  is formed. Crystallisation is sometimes slow, but may be accelerated by scratching the interior of the vessel with a glass rod.

Place a drop of the test solution on a spot plate, add a small crystal of ammonium thiocyanate followed by a little solid cobalt acetate. A blue colour is produced.

Sensitivity: 0.5  $\mu$ g. Hg. Concentration limit: 1 in 100,000.

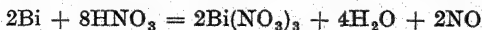
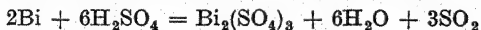
## Dry Test

All compounds of mercury when heated with a large excess (7–8 times the bulk) of anhydrous sodium carbonate in a small dry test-tube yield a grey mirror, consisting of fine drops of mercury, in the upper part of the tube. The globules coalesce when they are rubbed with a glass rod.

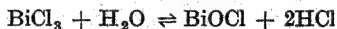
*Note.*—Mercury vapour is extremely poisonous, and not more than 0.1 gram of the substance should be used in the test.

## BISMUTH, Bi

Bismuth is a brittle, crystalline and reddish-white metal. It is insoluble in hydrochloric acid, but dissolves in hot concentrated sulphuric acid and in aqua regia. The best solvent is nitric acid.



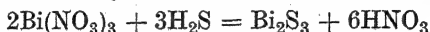
The salts of bismuth may be regarded as derived from the sesquioxide  $\text{Bi}_2\text{O}_3$ . The hydroxide  $\text{Bi}(\text{OH})_3$  is a weak base; the salts are accordingly hydrolysed by much water (see Hydrolysis of Salts, Section I, 40) yielding insoluble basic (usually bismuthyl, i.e. containing the radical  $\text{BiO}-$ ) salts.



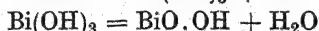
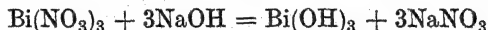
### III, 7. REACTIONS OF THE BISMUTH ION, $\text{Bi}^{+++}$

Use a solution of bismuth nitrate,  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , to which just sufficient nitric acid has been added to produce a clear solution.

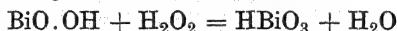
**1. Hydrogen Sulphide:** brown precipitate of bismuth sulphide  $\text{Bi}_2\text{S}_3$ , insoluble in cold dilute acids and in ammonium sulphide solution, but soluble in hot dilute nitric acid and in boiling concentrated hydrochloric acid.



**2. Sodium Hydroxide Solution:** white precipitate of bismuth hydroxide  $\text{Bi}(\text{OH})_3$  in the cold, very slightly soluble in excess of the reagent (2–3 mg. Bi in 100 ml. *N* NaOH solution), soluble in acids. It becomes yellow on boiling, due to partial dehydration.

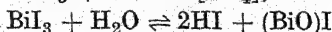
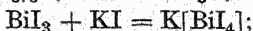
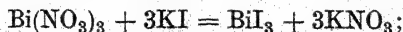


If hydrogen peroxide be added to the solution containing the white or yellowish-white precipitate in suspension, brown bismuthic acid  $\text{HBiO}_3$  is formed:

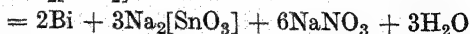
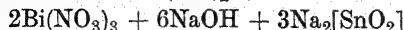


**3. Ammonia Solution:** a white basic salt, of variable composition, is precipitated. The precipitate is insoluble in excess of the reagent (distinction from copper and cadmium).

**4. Potassium Iodide Solution:** dark brown precipitate of bismuth tri-iodide, readily soluble in excess of the reagent to give a yellow solution of the complex salt  $\text{K}[\text{BiI}_4]$ . The complex is decomposed upon dilution giving first a precipitate of the tri-iodide and then an orange-coloured precipitate of the basic bismuthyl iodide  $(\text{BiO})\text{I}$ .

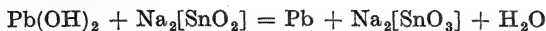


**5. Sodium Stannite Solution:** black precipitate of finely divided bismuth in the cold. The reagent is prepared by adding sodium hydroxide solution to a solution of stannous chloride until the initial white precipitate of stannous hydroxide just dissolves.





† The test is rendered more sensitive by making use of the fact that the slow reaction between lead hydroxide or sodium plumbite and sodium stannite is greatly accelerated by the separation of even minute quantities of bismuth:



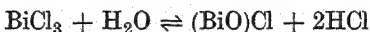
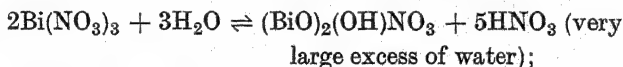
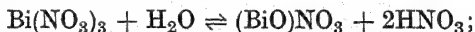
Silver, copper and mercury interfere: copper is rendered innocuous by the addition of a little potassium cyanide.

On a spot plate, mix a drop of the test solution, a drop of saturated lead chloride solution, a drop of 5 per cent potassium cyanide solution and 2 drops of sodium stannite solution. A brown to black coloration appears.

Sensitivity: 0.01  $\mu\text{g}$ . Bi. Concentration limit: 1 in 5,000,000.

The **sodium stannite reagent** is prepared by mixing just before use equal volumes of the two solutions *a* and *b*: (*a*) a solution of 0.5 g. of stannous chloride in 0.5 ml. of concentrated hydrochloric acid, diluted to 10 ml. with distilled water; (*b*) 25 per cent sodium hydroxide solution.

**6. Water.** When a solution of a bismuth salt is poured into a large volume of water, a white precipitate of the corresponding basic salt is produced, which is soluble in dilute mineral acids, but is insoluble in a solution of tartaric acid (distinction from antimony) and in solutions of alkali hydroxides (distinction from tin).



**7. Pyrogallol Reagent** { 1 : 3 : 5-trihydroxybenzene,  $\text{C}_6\text{H}_5(\text{OH})_3$  } : the addition of a slight excess of a concentrated solution of the reagent to a hot solution of a bismuth salt faintly acid with dilute hydrochloric acid or nitric acid, yields a yellow precipitate of the complex  $\text{Bi}(\text{C}_6\text{H}_3\text{O}_3)_3$ . It is best to add ammonia solution until the solution is alkaline to litmus paper and then dilute nitric acid until just acid. The test is a very sensitive one. Antimony interferes and should be absent.

The reagent is prepared as required: a suitable concentration is 0.5 gram of pyrogallol in 5 ml. of water.

**8. Sodium Phosphate or Sodium Arsenate Solution:** white crystalline precipitate of  $\text{BiPO}_4$  or  $\text{BiAsO}_4$ , sparingly soluble in dilute mineral acids (distinction from mercuric, lead, copper and cadmium salts).

†9. **Cinchonine-Potassium Iodide Reagent:** orange-red coloration or precipitate, due to bismuth-cinchonine iodide ( $\text{BiI}_3$ , cinchonine, HI), in faintly acid solution.

Moisten a piece of drop-reaction paper with the reagent and place a drop of the slightly acid test solution upon it. An orange-red spot is obtained.

Sensitivity: 0.15  $\mu\text{g}$ . Bi. Concentration limit: 1 in 350,000.

The test may also be carried out on a spot plate.

Lead, copper and mercury salts interfere because they react with the iodide. Nevertheless, bismuth may be detected in the presence of salts of these metals as they diffuse at different rates through the capillaries of the paper, and are fixed in distinct zones. When a drop of the test solution containing bismuth, lead, copper and mercury ions is placed upon absorbent paper impregnated with the reagent, four zones can be observed: (i) a white central ring, containing the mercury; (ii) an orange ring, due to bismuth; (iii) a yellow ring of lead iodide; and (iv) a brown ring of iodine liberated by the reaction with copper. The thicknesses of the rings will depend upon the relative concentrations of the various metals.

Sensitivity: 10–15  $\mu\text{g}$ . Bi.

The reagent is prepared by dissolving 1 g. of cinchonine in 100 ml. of hot water containing a few drops of nitric acid; after cooling, 2 g. of potassium iodide are added.

†10. **Thiourea Reagent** ( $\text{NH}_2\cdot\text{CS}\cdot\text{NH}_2$ ): intense yellow coloration in the presence of dilute nitric acid. The test may be carried out on drop-reaction paper, on a spot plate, or in a micro test-tube.

Sensitivity: 6  $\mu\text{g}$ . Bi. Concentration limit: 1 in 30,000.

Mercurous mercury, silver, antimony, ferric iron and chromates interfere and should therefore be absent.

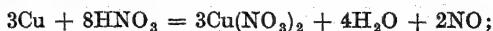
The reagent consists of a 10 per cent aqueous solution of thiourea.

## Dry Test

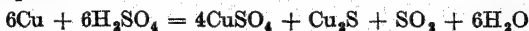
*Blowpipe test.*—When a bismuth compound is heated on charcoal with sodium carbonate in the blowpipe flame, a brittle bead of metal, surrounded by a yellow incrustation of the oxide, is obtained.

## COPPER, Cu

Copper is a light red metal, which is soft, malleable and ductile. It is unaffected by hydrochloric acid and by dilute sulphuric acid, but is readily attacked by dilute nitric acid and by warm concentrated sulphuric acid:



Some cuprous sulphide  $\text{Cu}_2\text{S}$  is also formed probably in accordance with the equation:



There are two series of copper compounds: those which may be regarded as derived from cuprous oxide  $\text{Cu}_2\text{O}$  (red), known as cuprous compounds and containing the ion  $\text{Cu}^+$ , and those similarly derived from cupric oxide  $\text{CuO}$  (black), known as the cupric compounds and giving rise to the ion  $\text{Cu}^{++}$ . The cuprous compounds, e.g.  $\text{CuCl}$ , are colourless, insoluble in water and comparatively unstable, being readily oxidised to the cupric compounds; they dissolve readily in concentrated solutions of halogen acids, forming colourless solutions which contain complex acids, such as  $\text{H}[\text{CuCl}_2]$ . Cupric salts, when dissolved in water, yield blue or green solutions; the anhydrous salts are white or yellow.

### III, 8. REACTIONS OF THE CUPRIC ION, $\text{Cu}^{++}$

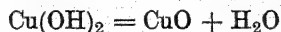
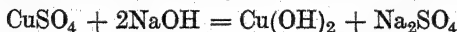
Use a solution of cupric sulphate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . (Aqueous solutions of cupric salts are blue, due to the ion  $[\text{Cu}(\text{H}_2\text{O})_4]^{++}$ ; the latter is usually written as  $\text{Cu}^{++}$ .)

**1. Hydrogen Sulphide:** a black precipitate of cupric sulphide  $\text{CuS}$  is obtained in neutral or preferably acid ( $\text{HCl}$ ) solutions. The precipitate is soluble in hot dilute nitric acid and in potassium cyanide solution; in the latter case a complex salt, potassium cupro-cyanide  $\text{K}_3[\text{Cu}(\text{CN})_4]$  is formed. Cupric sulphide is insoluble in boiling dilute sulphuric acid (distinction from cadmium); it is also insoluble in potassium hydroxide solution, in alkali monosulphide solution and very slightly soluble in alkali polysulphide solution.



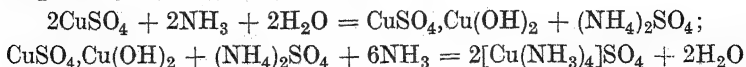
Cupric sulphide tends to form a colloidal solution and pass through filter paper. This is avoided by carrying out the precipitation in the presence of hydrochloric acid or some other electrolyte. It also tends to oxidise to the soluble sulphate when exposed to the air in the moist state; this is prevented by washing the precipitate with acidulated hydrogen sulphide water.

**2. Sodium Hydroxide Solution:** blue precipitate of cupric hydroxide  $\text{Cu}(\text{OH})_2$ , insoluble in moderate excess of the reagent, and converted on boiling into black cupric oxide.

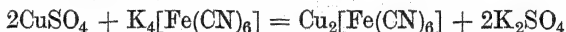


In the presence of a solution of tartaric acid or of citric acid, cupric hydroxide is not precipitated by solutions of caustic alkalis, but the solution is coloured an intense blue. If the alkaline solution is treated with certain reducing agents, such as hydroxylamine, hydrazine, glucose and acetaldehyde, yellow cuprous hydroxide is precipitated from the warm solution, which is converted into red cuprous oxide  $\text{Cu}_2\text{O}$  on boiling. The alkaline solution of cupric salt containing tartaric acid is usually known as *Fehling's solution*; it contains the complex salt  $\text{Na}_2[(\text{OOC} \cdot \text{CHO})_2\text{Cu}]$ .

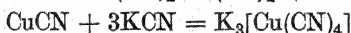
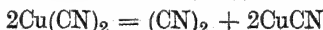
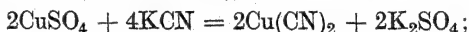
**3. Ammonia Solution:** pale blue precipitate of basic salt, soluble in excess of the precipitant with the formation of a deep blue solution containing the complex salt, tetra-ammine cupric sulphate  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ .



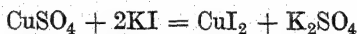
**4. Potassium Ferrocyanide Solution:** reddish-brown precipitate of cupric ferrocyanide  $\text{Cu}_2[\text{Fe}(\text{CN})_6]$  from neutral or acid solutions. It is insoluble in dilute acids, but dissolves in aqueous ammonia forming a blue solution. The precipitate is decomposed by solutions of alkali hydroxides with the separation of blue cupric hydroxide.



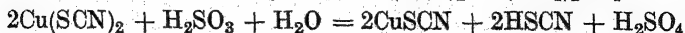
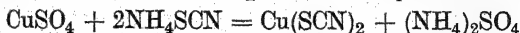
**5. Potassium Cyanide Solution** (*highly poisonous*): yellow precipitate of cupric cyanide  $\text{Cu}(\text{CN})_2$ , which quickly decomposes into cuprous cyanide  $\text{CuCN}$  and cyanogen  $(\text{CN})_2$ . The cuprous cyanide dissolves in excess of the reagent forming a colourless solution of a complex salt, potassium cuprocyanide  $\text{K}_3[\text{Cu}(\text{CN})_4]$ , in which the concentration of copper ions is so small that it is insufficient to give a precipitate with hydrogen sulphide (distinction from cadmium) (for detailed explanation see Complex Ions, Section I, 20).



**6. Potassium Iodide Solution:** cupric iodide  $\text{CuI}_2$  is first precipitated; this immediately decomposes into white cuprous iodide  $\text{CuI}$  and free iodine. The latter dissolves in the excess of the potassium iodide solution and colours the solution brown.



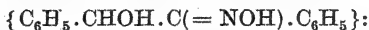
**7. Potassium or Ammonium Thiocyanate Solution:** black precipitate of cupric thiocyanate  $\text{Cu}(\text{SCN})_2$ , which passes slowly, or immediately upon adding sulphurous acid solution, into white cuprous thiocyanate  $\text{CuSCN}$ . The latter is insoluble in water and in dilute sulphuric and hydrochloric acids.



8. **Iron.** If a clean iron nail or the blade of a pen-knife is immersed in a solution of a cupric salt, a red deposit of copper is obtained (see Electrode Potentials, Section I, 29):



†9.  **$\alpha$ -Benzoin Oxime (or Cupron) Reagent**



green precipitate of copper benzoin oxime  $\text{Cu}(\text{C}_{14}\text{H}_{11}\text{O}_2\text{N})$ , insoluble in dilute ammonia solution. In the presence of metallic salts which are precipitated by ammonia solution, their precipitation can be prevented by the addition of sodium potassium tartrate. The reagent is specific for copper in ammoniacal tartrate solution. Large amounts of ammonium salts interfere and should be removed by evaporation and heating to glowing: the residue is then dissolved in a little dilute hydrochloric acid.

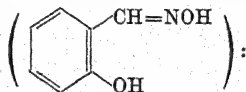
Treat some drop-reaction paper with a drop of the weakly acid test solution and a drop of the reagent, and then hold it over ammonia vapour. A green coloration is obtained.

Sensitivity: 0.1  $\mu\text{g}$ . Cu. Concentration limit: 1 in 500,000.

If other ions, precipitable by ammonia solution, are present, a drop of 10 per cent Rochelle salt solution is placed upon the paper before the reagent is added.

The reagent is prepared by dissolving 5 g. of  $\alpha$ -benzoin oxime in 100 ml. of 95 per cent alcohol.

†10. **Salicylaldoxime Reagent**



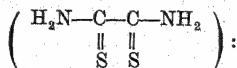
greenish-yellow precipitate of copper salicylaldoxime  $\text{Cu}(\text{C}_7\text{H}_5\text{O}_2\text{N})_2$  in acetic acid solution, soluble in mineral acids. Only palladium and gold give precipitates  $\{\text{Pd}(\text{C}_7\text{H}_5\text{O}_2\text{N})_2$  and metallic gold respectively} in acetic acid solution and should therefore be absent.

Place a drop of the test solution, which has been neutralised and then acidified with acetic acid, in a micro test-tube and add a drop of the reagent. A yellow-green precipitate or opalescence (according to the amount of copper present) is obtained.

Sensitivity: 0.5  $\mu\text{g}$ . Cu. Concentration limit: 1 in 100,000.

The reagent is prepared by dissolving 1 g. of salicylaldoxime in 5 ml. of cold alcohol and pouring the solution dropwise into 95 ml. of water at a temperature not exceeding  $80^\circ\text{C}$ ; the mixture is shaken until clear, and filtered if necessary.

†11. **Rubeanic Acid (or Dithio-oxamide) Reagent**



black precipitate of copper rubeanate  $\text{Cu}\{\text{C}(=\text{NH})\text{S}\}_2$  from ammoniacal or weakly acid solution. The precipitate is formed in the

presence of alkali tartrates, but not in alkali-cyanide solutions. Only nickel and cobalt ions react under similar conditions yielding blue and brown precipitates respectively. Copper may, however, be detected in the presence of these elements by utilising the *capillary separation method* upon filter paper. Mercurous mercury should be absent as it gives a black stain with ammonia.

Place a drop of the neutral test solution upon drop-reaction paper, expose it to ammonia vapour and add a drop of the reagent. A black or greenish-black spot is produced.

Sensitivity: 0.01  $\mu\text{g}$ . Cu. Concentration limit: 1 in 2,500,000.

Traces of copper in distilled water give a positive reaction, hence a blank test must be carried out with the distilled water.

In the **presence of nickel**, proceed as follows. Impregnate drop reaction paper with the reagent and add a drop of the test solution acidified with acetic acid. Two zones or circles are formed: the central olive green or black ring is due to copper and the outer blue-violet ring to nickel.

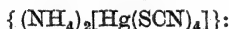
Sensitivity: 0.05  $\mu\text{g}$ . Cu in the presence of 20,000 times amount of Ni.  
Concentration limit: 1 in 1,000,000.

In the **presence of cobalt**, the central green or black ring, due to copper, is surrounded by a yellow-brown ring of cobalt rubeanate.

Sensitivity: 0.25  $\mu\text{g}$ . Cu in the presence of 2,000 times amount of Co.  
Concentration limit: 1 in 200,000.

The **reagent** consists of a 0.5 per cent solution of rubeanic acid in 95 per cent ethyl alcohol. It does not keep well and should be prepared as required.

### †12. Ammonium Mercuri-thiocyanate Reagent



deep violet, crystalline precipitate in the presence of zinc or cadmium ions. Cobalt and nickel interfere since they yield green or blue precipitates of the corresponding mercuri-thiocyanates  $\text{X}[\text{Hg}(\text{SCN})_4]$ ; the interference of ferric iron is avoided by carrying out the precipitation in the presence of alkali fluorides or oxalates.

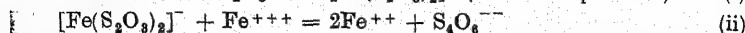
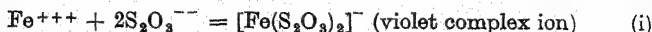
Place a drop of the acid test solution upon a spot plate, add 1 drop of 1 per cent zinc acetate solution and 1 drop of the reagent. The precipitated zinc mercuri-thiocyanate is coloured violet due to coprecipitation of the copper complex: it may be regarded as  $\text{Zn}[\text{Hg}(\text{SCN})_4] + \text{Cu}[\text{Hg}(\text{SCN})_4]$ .

Sensitivity: 0.1  $\mu\text{g}$ . Cu. Concentration limit: 1 in 500,000.

(The addition of copper ions to a precipitate of zinc mercuri-thiocyanate, already formed, has no influence.)

The **reagent** is prepared by dissolving 9 g. of ammonium thiocyanate and 8 g. of mercuric chloride in 100 ml. of water.

†13. Catalytic Effect upon the Ferric Iron-Thiosulphate Reaction.—Ferric salts react with thiosulphates in accordance with the equations:



Reaction (i) is fairly rapid; reaction (ii) is a slow one, but is enormously accelerated by traces of copper salts. If the reaction is carried out in the presence of a thiocyanate, which serves as an indicator for the presence of ferric iron and also retards reaction (ii), then the reaction velocity, which is proportional to the time taken for complete decolorisation, may be employed for detecting minute amounts of cupric ions. Tungsten and, to a lesser extent, selenium cause a catalytic acceleration similar to that of copper: they should therefore be absent.

Upon adjacent cavities of a spot plate place a drop of the test solution and a drop of distilled water. Add to each 1 drop of the ferric thiocyanate reagent and 3 drops of 0.1N-sodium thiosulphate solution. The decolorisation of the copper-free solution is complete in 1.5–2 minutes: if the test solution contains 1  $\mu$ g. of copper, the decolorisation is instantaneous. For smaller amounts of copper, the difference in times between the two tests is still appreciable.

Sensitivity: 0.02  $\mu$ g. Cu. Concentration limit: 1 in 2,500,000.

The “ferric thiocyanate” reagent is prepared by dissolving 1.5 g. of ferric chloride and 2.0 g. of potassium thiocyanate in 100 ml. of water.

## Dry Tests

(i) *Blowpipe test*.—When copper compounds are heated with alkali carbonate upon charcoal, red metallic copper is obtained, but no oxide is visible.

(ii) *Borax bead*.—Green while hot and blue when cold after heating in the oxidising flame; red in the reducing flame, best obtained by the addition of a trace of tin or by moistening with stannous chloride solution.

(iii) *Flame test*.—Green especially in the presence of halides, e.g. by moistening with concentrated hydrochloric acid before heating.

## CADMIUM, Cd

Cadmium is a silver-white, malleable and ductile metal. It dissolves slowly in dilute hydrochloric and sulphuric acids with the evolution of hydrogen. The best solvent for the metal is nitric acid. Only one series of salts, derived from the oxide CdO, is of importance in qualitative analysis.

## III, 9. REACTIONS OF THE CADMIUM ION, Cd<sup>++</sup>

Use a solution of cadmium sulphate, 3CdSO<sub>4</sub>·8H<sub>2</sub>O.

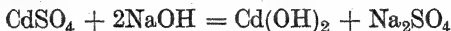
1. **Hydrogen Sulphide**: yellow precipitate of cadmium sulphide CdS from solutions acidified with a *little* hydrochloric acid (strength approximately 0.3 molar). The precipitate is soluble in hot dilute nitric acid and also in hot dilute sulphuric acid (distinction from copper), but is insoluble in potassium cyanide solution (difference from copper). No precipitation

takes place in strongly acid solutions owing to the reversibility of the reaction:

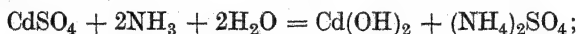


(for a detailed discussion of the reaction see Section I, 16).

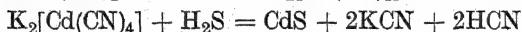
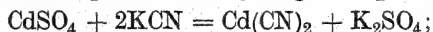
**2. Sodium Hydroxide Solution:** white precipitate of cadmium hydroxide  $\text{Cd}(\text{OH})_2$ , insoluble in excess of the reagent.



**3. Ammonia Solution:** white precipitate of cadmium hydroxide, soluble in excess of the precipitant (distinction from lead and bismuth); the soluble complex salt, tetra-ammine cadmium sulphate  $[\text{Cd}(\text{NH}_3)_4]\text{SO}_4$ , is formed (see Complex Ions, Section I, 20).



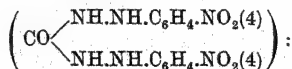
**4. Potassium Cyanide Solution:** white precipitate of cadmium cyanide  $\text{Cd}(\text{CN})_2$ , soluble in excess of the reagent to yield the complex, potassium cadmi-cyanide  $\text{K}_2[\text{Cd}(\text{CN})_4]$ . A sufficiently high concentration of cadmium ions is produced by the dissociation of the complex ion to give a precipitate of yellow cadmium sulphide with hydrogen sulphide.



The marked difference in the values of the instability constants of the complex ions  $[\text{Cd}(\text{CN})_4]^{--}$  and  $[\text{Cu}(\text{CN})_4]^{--}$  serves as the basis for one of the methods for the separation of copper and cadmium (for discussion, see Section I, 20).

**5. Ammonium Thiocyanate Solution:** no precipitate (distinction from copper).

#### †6. Dinitro-*p*-diphenylcarbazine Reagent



Cadmium hydroxide is coloured brown by the reagent, which rapidly becomes greenish-blue with formaldehyde.

Place a drop of the acid, neutral or ammoniacal test solution on a spot plate and mix it with 1 drop of 10 per cent sodium hydroxide solution and 1 drop of 10 per cent potassium cyanide solution. Introduce 1 drop of the reagent and 2 drops of 40 per cent formaldehyde solution. A brown precipitate is formed, which very rapidly becomes greenish-blue. The reagent alone is red in alkaline solution and is coloured violet with formaldehyde, hence it is advisable to compare the



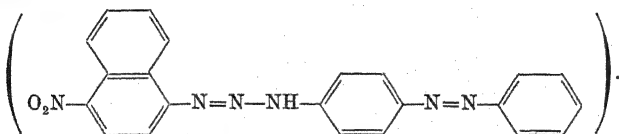
colour produced in a blank test with pure water when searching for minute amounts of cadmium.

Sensitivity: 0.8  $\mu\text{g}$ . Cd. Concentration limit: 1 in 60,000.

In the presence of considerable amounts of copper, 3 drops each of the potassium cyanide and formaldehyde solution should be used; the sensitivity is 4  $\mu\text{g}$ . Cd in the presence of 400 times the amount of Cu.

The reagent consists of a 0.1 per cent solution of dinitro-*p*-diphenylcarbazide in alcohol.

†7. 4-Nitronaphthalene-diazoamino-azobenzene ("Cation 2B")  
Reagent



Cadmium hydroxide forms a red-coloured lake with the reagent, which contrasts with the blue tint of the latter.

Place a drop of the reagent upon drop reaction paper, add one drop of the test solution (which should be slightly acidified with acetic acid containing a little sodium potassium tartrate), and then one drop of 2N potassium hydroxide. A bright pink spot, surrounded by a blue circle, is produced.

Sensitivity: 0.025  $\mu\text{g}$ . Cd.

The interference of Cu, Ni, Co, Fe, Cr and Mg is prevented by adding sodium potassium tartrate to the test solution: only Ag (removed as AgI by the addition of a little KI solution) and Hg then interfere. Mercury is best removed by adding a little sodium potassium tartrate, a few crystals of hydroxylamine hydrochloride, followed by KOH solution until alkaline; the mercury is precipitated as metal. Stannous chloride is not suitable for this reduction since most of the cadmium is adsorbed on the mercury precipitate.

The reagent is prepared by dissolving 0.02 g. of "cation 2B" in 100 ml. of ethyl alcohol to which 1 ml. of 2N-KOH is added. The solution must *not* be warmed. It is destroyed by mineral acid.

## Dry Tests

*Blowpipe test.*—All cadmium compounds when heated with alkali carbonate on charcoal give a brown incrustation of cadmium oxide CdO.

*Ignition test.*—Cadmium salts are reduced by sodium oxalate to elementary cadmium, which is usually obtained as a metallic mirror surrounded by a little brown cadmium oxide. Upon heating with sulphur, the metal is converted into yellow cadmium sulphide.

Place a little of the cadmium salt mixed with an equal weight of sodium oxalate in a small ignition tube, and heat. A mirror

of metallic cadmium with brown edges is produced. Allow to cool, add a little flowers of sulphur and heat again. The metallic mirror is gradually converted into the orange-coloured sulphide, which becomes yellow after cooling. Do not confuse this with the yellow sublimate of sulphur.

DETECTION AND SEPARATION OF THE METALS IN THE COPPER  
GROUP (GROUP IIA)

The foregoing reactions of the metals of the copper group furnish the facts upon which the table of separation is based (Tables II or IIA). The student should use the test solution provided, or else prepare a solution of the chlorides of the metals and work through the table. The sulphides of the metals of this group, and also those of arsenic, antimony and tin (Group IIB), are precipitated by hydrogen sulphide in the presence of dilute hydrochloric acid. The reactions of the Group IIB metals will be studied later, but for the present it will suffice to state that the sulphides of the Group IIA metals are best separated from those of Group IIB by the solubility of the latter in warm yellow ammonium sulphide solution or in hot 2*N* potassium hydroxide solution.

### III, 10. Table II. Analysis of the Copper Group (Group IIA)

The ppt. obtained with  $H_2S$  in the presence of dilute  $HCl$  (ca. 0.3*N*) may contain the sulphides  $HgS$ ,  $PbS$ ,  $Bi_2S_3$ ,  $CuS$ ,  $CdS$  and also  $SnS$ ,  $SnS_2$ ,  $Sb_2S_3$  and  $As_2S_3$ . (T) Pierce the point of the filter with a small glass rod, wash the ppt. into a beaker with a small quantity of water. Add 5 ml. of yellow ammonium sulphide solution, heat to 50–60° for 2–3 minutes, and filter. Wash the residue with a little dilute (1 : 100)  $(NH_4)_2S_x$  solution.

**Residue.** May contain  $HgS$ ,  $PbS$ ,  $Bi_2S_3$ ,  $CdS$  and  $CuS$ . Transfer the ppt. to a beaker or porcelain basin, add ca. 5 ml. of dilute  $HNO_3$ , boil for a few minutes, filter and wash with a little water.

**Filtrate.** May contain metals of Group IIB. (See Table III.)

**Residue.**  
Black:  $HgS$ .  
Warm the ppt. with conc.  $HCl$ , add bromine water dropwise until most or all of ppt. dissolves. Boil off any excess of bromine.

Filter if necessary, dilute with an equal volume of water, and add  $SnCl_2$  solution. White ppt., turning grey or black.

**Hg present.**  
Alternatively, dissolve the ppt. in  $NaOCl$ - $HCl$ , etc., as detailed in Table IIA.

**Filtrate.** May contain  $Pb(NO_3)_2$ ,  $Bi(NO_3)_3$ ,  $Cu(NO_3)_2$  and  $Cd(NO_3)_2$ . Test a small portion for  $Pb$  by adding dilute  $H_2SO_4$  and alcohol; a white ppt. indicates  $Pb$ . If  $Pb$  is present, add dilute  $H_2SO_4$  and concentrate in the fume chamber until thick white fumes appear. Cool, dilute with 10 ml. of water, and filter. Wash with a little cold water.

**Residue.**  
White:  $PbSO_4$ .  
Pass 2 ml. of ammonium acetate solution through the filter several times. Treat filtrate with a few drops of dilute acetic acid and then with  $K_2CrO_4$  solution.  
Yellow ppt. of  $PbCrO_4$ .

**Pb present.**

**Filtrate.** May contain  $Bi^{+++}$ ,  $Cu^{++}$  and  $Cd^{++}$ . Add  $NH_3$  solution in excess, and filter.

**Residue.**  
White:  $Bi(OH)_3$ .  
Wash well, pour sodium stannite solution on filter. Blackening of ppt.

**Bi present.**  
Alternatively, dissolve the white ppt. in dilute  $HNO_3$  or in dilute  $HCl$ , and add a little thiourea solution.

Yellow coloration.  
**Bi present.**

**Filtrate.** May contain  $[Cu(NH_3)_4]^{++}$  and  $[Cd(NH_3)_4]^{++}$ . If colourless,  $Cu$  is absent; test then directly for  $Cd$  with  $H_2S$  (see below). If blue,  **$Cu$  present.**

Divide the solution into two unequal parts.

*Smaller portion* (1). Add  $K_4[Fe(CN)_6]$  solution and acetic acid. Reddish-brown ppt.

**$Cu$  present.**  
*Larger portion.*  
Add  $KCN$  solution dropwise until solution is decolorised. Pass  $H_2S$  for 10–20 seconds.

### III, 10. Table IIA. Analysis of the Copper Group (Group IIA)

The ppt. obtained with  $H_2S$  in the presence of dilute  $HCl$  (ca. 0.3N) may contain the sulphides  $HgS$ ,  $PbS$ ,  $Bi_2S_3$ ,  $CuS$ ,  $CdS$  and also  $As_2S_3$ ,  $Sb_2S_3$  and  $SnS_2$  (1). (T) Pierce the point of the filter with a small glass rod, wash the ppt. into a beaker with a *small* quantity of water. Add 10 ml. of 2N-potassium hydroxide and boil with *constant stirring* for 2–3 minutes (*CAUTION*: see Note 2). Add 2 ml. of freshly-prepared saturated  $H_2S$  water: stir and filter (preferably through a double filter). Wash the residue twice with a little water and collect the washings with the filtrate.

**Residue.** May contain  $HgS$ ,  $PbS$ ,  $Bi_2S_3$ ,  $CdS$  and  $CuS$ . Transfer the ppt. to a small beaker or porcelain basin, add ca. 5 ml. of dilute  $HNO_3$ , boil gently for a few minutes, filter and wash with a little water.

**Filtrate.** May contain metals of Group IIB. (See Table III, Section III, 18.)

**Residue.** Black:  $HgS$ . Dissolve in a mixture of 2.5 ml. of 10%  $NaOCl$  solution and 0.5 ml. of dilute  $HCl$ . Add 1 ml. of dilute  $HCl$ , boil off excess of  $Cl_2$  and cool. Add  $SnCl_2$  solution. White ppt. turning grey or black.

**Hg (ic) present.**

**Filtrate.** May contain  $Pb(NO_3)_2$ ,  $Bi(NO_3)_3$ ,  $Cu(NO_3)_2$  and  $Cd(NO_3)_2$ . Add excess of concentrated  $NH_3$  solution until precipitation is complete. Filter.

**Residue.** May contain  $Bi(OH)_3$  and  $Pb(OH)_2$ . Warm with 5 ml. of  $NaOH$  solution and filter.

**Residue.** May be  $Bi(OH)_3$ . Wash with a little water. Pour sodium stannite solution over filter. Blackening of ppt.

**Bi present.** Alternatively, dissolve a little of the ppt. in 2–3 drops of dilute  $HNO_3$ ; place 1 drop of this solution upon filter paper moistened with cinchonine-potassium iodide reagent.

Orange-red spot.  
**Bi present.**

**Filtrate.** May contain sodium plumbite  $Na_2[PbO_2]$ . Acidify with dilute acetic acid and add  $K_2CrO_4$  solution. Yellow ppt. of  $PbCrO_4$ .  
**Pb present.**

**Filtrate.** May contain  $[Cu(NH_3)_4]^{++}$  and  $[Cd(NH_3)_4]^{++}$ . If colourless, Cu is absent; test then directly for Cd by passing  $H_2S$  for 10–20 seconds into the ammoniacal solution.

Yellow ppt. of  $CdS$ .  
**Cd present.**

If blue, **Cu present.** Divide the solution into two unequal parts.

*Smaller portion.* Acidify with dilute acetic acid and add  $K_4[Fe(CN)_6]$  solution.

Reddish-brown ppt.  
**Cu present (3).**

*Larger portion.* Add  $KCN$  solution dropwise until solution is decolourised. Pass  $H_2S$  for 10–20 seconds.

Immediate yellow ppt. of  $CdS$ .

**Cd present (4).**

### III, 10. Table SMIIA. Analysis of the Copper Group (Group IIA)

<p>The ppt. obtained with <math>H_2S</math> in the presence of dilute <math>HCl</math> (ca. 0.3N) may contain the sulphides <math>HgS</math>, <math>PbS</math>, <math>Bi_2S_3</math>, <math>CuS</math> and <math>CdS</math>, and also <math>As_2S_3</math>, <math>Sb_2S_3</math> and <math>SnS_2</math> (1). Treat the ppt. with 1.5 ml. of 2N <math>KOH</math> solution, and heat in a boiling water bath for 3 minutes with occasional stirring (<i>CAUTION</i>: see Note 2). Add 4 drops of freshly-prepared saturated <math>H_2S</math> water; stir and centrifuge.</p>			
<p><b>Residue.</b> May contain <math>HgS</math>, <math>PbS</math>, <math>Bi_2S_3</math>, <math>CuS</math> and <math>CdS</math>. Wash the residue once with 0.5 ml. of water and combine the washings with the first centrifugate. Treat the ppt. with 1–1.5 ml. of dilute <math>HNO_3</math>; place in a boiling water bath, and heat for 2–3 minutes with stirring. Centrifuge.</p>		<p><b>Centrifugate.</b> May contain metals of Group IIB. (See Table SMIIA, Section III, 18.)</p>	
<p><b>Residue.</b> Black: <math>HgS</math>. Wash with 0.5 ml. of water and discard the washings. Treat the ppt. with 5 drops of 10% <math>NaOCl</math> solution and 1 drop of dilute <math>HCl</math>. Heat on the water bath for 1 minute. To the clear solution, add 1–2 drops of <math>SnCl_2</math> solution. White ppt., turning grey or black. <b>Hg (ic) present.</b></p>		<p><b>Centrifugate.</b> May contain <math>Pb(NO_3)_2</math>, <math>Bi(NO_3)_3</math>, <math>Cu(NO_3)_2</math> and <math>Cd(NO_3)_2</math>. Add excess of concentrated <math>NH_3</math> solution, and centrifuge.</p>	
<p><b>Residue.</b> May contain <math>Bi(OH)_3</math> and <math>Pb(OH)_2</math>. Add 1 ml. of <math>NaOH</math> solution, place in the boiling water rack for 2 minutes, and centrifuge.</p>		<p><b>Centrifugate.</b> May contain <math>[Cu(NH_3)_4](NO_3)_2</math> and <math>[Cd(NH_3)_4](NO_3)_2</math>. If colourless, <math>Cu</math> is absent: test then directly for <math>Cd</math> by passing <math>H_2S</math> for 10 seconds into the ammoniacal solution. Yellow ppt. of <math>CdS</math>.</p>	
<p><b>Residue.</b> May be <math>Bi(OH)_3</math>. Wash with 0.5 ml. of water and reject washings. Add 1 ml. of sodium stannite reagent (3) to the ppt. Immediate blackening of ppt. <b>Bi present.</b> Alternatively, dissolve a little of the ppt. in 1–2 drops of dilute <math>HNO_3</math>. Place 1 drop of the solution upon filter paper moistened with cinchonine-potassium iodide reagent. Orange-red spot. <b>Bi present.</b></p>		<p><b>Centrifugate.</b> May contain <math>Na_2[PbO_2]</math>. Acidify with dilute acetic acid, add 2 drops of <math>K_2CrO_4</math> solution. Yellow ppt. of <math>PbCrO_4</math>. <b>Pb present.</b></p>	
		<p><b>Cd present.</b> If blue, <math>Cu</math> is present. Divide into two unequal parts. <i>Smaller portion</i> (4). Acidify with acetic acid and add 1 drop of <math>K_4[Fe(CN)_6]</math> solution. Reddish-brown ppt. on standing for 2–3 minutes.</p>	
		<p><b>Cu present.</b> <i>Larger portion.</i> Add <math>KCN</math> solution dropwise, with stirring, until the blue colour is discharged. Pass <math>H_2S</math> for 30–40 seconds. Yellow ppt. of <math>CdS</math>.</p>	
		<p><b>Cd present.</b> Confirm <math>Cd</math> by ignition test with <math>Na_2C_2O_4</math>, etc.</p>	

## NOTES TO TABLE II

*Notes.* (1) Alternatively, just acidify a few drops of the solution with dilute sulphuric acid. Add one drop of the acid solution to a few drops of zinc sulphate or acetate solution, and then add a little ammonium mercuri-thiocyanate reagent. A violet precipitate confirms Cu. If a little amyl alcohol is added, the precipitate collects in and colours the organic layer.

(2) Cadmium may be confirmed, if desired, by the ignition test with sodium oxalate, etc. (see Section III, 9, *Dry Tests*).

## NOTES TO TABLE IIA

*Notes.* (1) Stannous sulphide  $\text{SnS}$  is not completely soluble in  $2N$  KOH. If tin is present in the stannous state, it is necessary to oxidise it with  $\text{H}_2\text{O}_2$ : a limited amount of arsenious arsenic may be oxidised at the same time.

(2) Potassium and sodium hydroxides are extremely dangerous substances because of their destructive effects upon the eyes. Precipitates, when heated with KOH solution, tend to bump. To avoid any possibility of the mixture spurting into the eyes with a consequent likely loss of sight, it is essential (a) to conduct the operation in a fume chamber, (b) to stir the mixture constantly and (c) to avoid bringing the face over the beaker. It is recommended that goggles be worn during this and similar operations.

(3) Alternatively, just acidify a few drops of the solution with dilute sulphuric acid. Add 1 drop of the acidic solution to a few drops of zinc sulphate or acetate solution, and then introduce a few drops of the ammonium mercuri-thiocyanate reagent. A violet precipitate confirms Cu. If a little amyl alcohol is added, the precipitate collects in and colours the organic layer. It is recommended that this test be performed even if the solution is almost colourless. A blue solution indicates that copper is present in quantity.

(4) Cadmium may be confirmed, if desired, by the ignition test with sodium oxalate, etc. (see Section III, 9, *Dry Tests*).

## NOTES TO TABLE SMIIA

*Notes.* (1) Stannous sulphide is not completely soluble in  $2N$  KOH solution. For this reason  $\text{H}_2\text{O}_2$  is employed in the Group Separation Table SM.S (Section VI, 9); any stannous tin is oxidised to the stannic state, leading ultimately to  $\text{SnS}_2$ , which dissolves readily in warm  $2N$  KOH.

(2) Great care should be taken in heating the KOH mixture. The mixture should be stirred constantly with a stirring rod: the face should not be brought directly over the heated tube. Potassium hydroxide solution is a dangerous substance because of its destructive action upon the eyes.

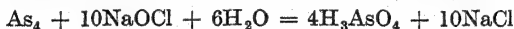
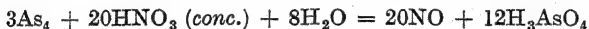
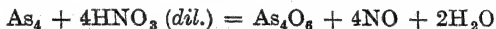
(3) The sodium stannite solution is prepared by treating 1-2 drops of  $\text{SnCl}_2$  solution with NaOH solution dropwise until the initial precipitate of  $\text{Sn(OH)}_2$  dissolves completely. Cooling is desirable.

(4) Alternatively, acidify with dilute  $\text{H}_2\text{SO}_4$ , add a drop or two of  $\text{ZnSO}_4$  solution, followed by a few drops of ammonium mercuri-thiocyanate reagent. A violet precipitate confirms Cu. The precipitate is rendered readily visible by adding a few drops of amyl alcohol and stirring; it collects in and colours the organic layer.

## THE ARSENIC GROUP (GROUP IIB)

## ARSENIC, As

Arsenic is a steel-grey, brittle solid with a metallic lustre. It sublimes on heating, and a characteristic, garlic-like odour is apparent; on heating in a free supply of air, arsenic burns with a blue flame yielding white fumes of arsenious oxide  $\text{As}_2\text{O}_3$ . *All arsenic compounds are poisonous.* The element is insoluble in hydrochloric acid and in dilute sulphuric acid: it dissolves readily in dilute nitric acid yielding arsenious oxide, and in concentrated nitric acid or in aqua regia or in sodium hypochlorite solution forming arsenic acid.

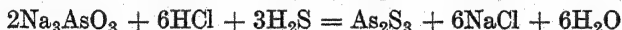
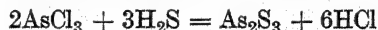


Two series of compounds of arsenic are commonly encountered: (a) The *arsenious* compounds may be regarded as derived from the amphoteric arsenious oxide  $\text{As}_2\text{O}_3$ , which yields salts with strong acids, e.g. arsenious chloride  $\text{AsCl}_3$ , and with strong bases, e.g. sodium arsenite  $\text{NaAsO}_2$ . (b) The *arsenic* compounds corresponding to the pentoxide  $\text{As}_2\text{O}_5$ ; they are usually salts of the tribasic ortho-arsenic acid, e.g.  $\text{NaH}_2\text{AsO}_4$ ,  $\text{Na}_2\text{HAsO}_4$  and  $\text{Na}_3\text{AsO}_4$ .

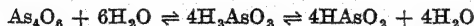
## III, 11. REACTIONS OF ARSENIOUS COMPOUNDS

Use a solution of arsenious oxide\* in hydrochloric acid, or a solution of sodium arsenite,  $\text{NaAsO}_2$ .†

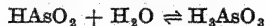
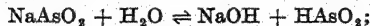
1. **Hydrogen Sulphide:** yellow precipitate of arsenious sulphide  $\text{As}_2\text{S}_3$  in acid (hydrochloric) solution.



\* Arsenious oxide is sparingly soluble in water yielding a solution containing the weak arsenous acid; the oxide, however, is recovered upon concentrating the solution.



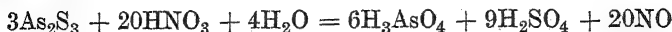
† The solid salt has the formula  $\text{NaAsO}_2$ ; i.e. sodium meta-arsenite. It is considerably hydrolysed in solution:



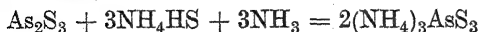
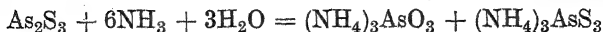
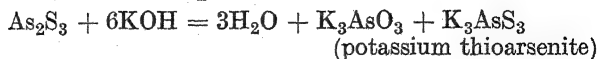
There is some evidence (e.g. the production of silver ortho-arsenite  $\text{Ag}_3\text{AsO}_3$ ) that the  $\text{AsO}_3^{--}$  is present in solution. For simplicity, the reactions of arsenites will be represented as derived from the ortho-arsenite ion  $\text{AsO}_3^{--}$  or, when written as molecular equations, from  $\text{Na}_3\text{AsO}_3$ . It should, however, be borne in mind that the meta-arsenite ion  $\text{AsO}_2^-$  may also be present in solution.

Similarly, the meta-thioarsenite ( $\text{AsS}_2^-$ ) and ortho-thioarsenite ( $\text{AsS}_3^{--}$ ) ions appear to exist in solution. The subject requires re-investigation.

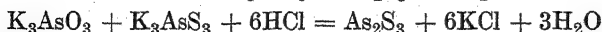
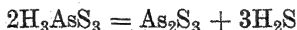
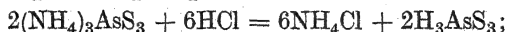
The precipitate is insoluble in concentrated hydrochloric acid (distinction and method of separation from  $\text{Sb}_2\text{S}_3$  and  $\text{SnS}_2$ ), but dissolves in hot concentrated nitric acid:



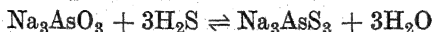
It is also readily soluble in solutions of alkali hydroxides, ammonia and ammonium sulphide:



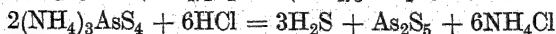
Upon acidifying the above solutions thioarsenious acid,  $\text{H}_3\text{AsS}_3$ , is set free: this acid is unstable in the free state and decomposes immediately into arsenious sulphide and hydrogen sulphide. Hence, upon treating a mixture of an arsenite and thioarsenite or a thioarsenite with dilute hydrochloric acid, arsenious sulphide is precipitated:



The formation of soluble thio-salts explains the non-precipitation of arsenious sulphide from solutions of arsenites in neutral or alkaline solution; for complete precipitation of arsenic as the trisulphide, sufficient free mineral acid must be present in the solution to prevent the formation of soluble thio-salts:



Arsenious sulphide dissolves readily in yellow ammonium sulphide solution  $(\text{NH}_4)_2\text{S}_x$  forming first ammonium thioarsenite  $(\text{NH}_4)_3\text{AsS}_3$ , which is then oxidised to the thioarsenate  $(\text{NH}_4)_3\text{AsS}_4$  by excess of sulphur. Upon acidifying the solution arsenic pentasulphide  $\text{As}_2\text{S}_5$  is precipitated, together with a little sulphur, produced by the decomposition of the excess of the ammonium polysulphide by the acid.



**2. Silver Nitrate Solution:** yellow precipitate of silver arsenite  $\text{Ag}_3\text{AsO}_3$  from *neutral* solutions (distinction from arsenates), soluble in ammonia solution and in nitric acid (compare Section I, 19).





**3. Magnesia Mixture** (a solution containing  $\text{MgCl}_2$ ,  $\text{NH}_4\text{Cl}$  and a little  $\text{NH}_3$ ): no precipitate (distinction from arsenate).

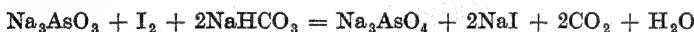
A similar result is obtained with the **magnesium nitrate reagent** (a solution containing  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{NH}_4\text{NO}_3$  and a little  $\text{NH}_3$ ).

**4. Copper Sulphate Solution:** green precipitate of copper arsenite (Scheele's green), variously formulated as  $\text{CuHAsO}_3$  and  $\text{Cu}_3(\text{AsO}_3)_2 \cdot x\text{H}_2\text{O}$ , from neutral solutions, soluble in acids, and also in ammonia solution forming a blue solution. The precipitate also dissolves in sodium hydroxide solution; upon boiling, cuprous oxide is precipitated.

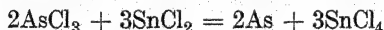
**5. Solution of Iodine in Potassium Iodide Solution:** decolourised, owing to the formation of hydriodic and arsenic acids.



The reaction is not a quantitative one because of the reducing character of the hydrogen iodide formed; in the presence of excess of sodium bicarbonate solution, which neutralises the hydriodic acid as formed, the reaction is quantitative. Sodium carbonate cannot be employed as this reacts with the iodine.



**6. Stannous Chloride Solution and Concentrated Hydrochloric Acid (Bettendorff's Test).**—A few drops of the arsenite solution are added to 2 ml. of concentrated hydrochloric acid and 0.5 ml. of saturated stannous chloride solution, and the solution gently warmed; the solution becomes dark brown and finally black, due to the separation of elementary arsenic.



If the test be made with the sulphide precipitated in acid solution, then only mercury will interfere; by converting the arsenic into magnesium ammonium arsenate and heating to redness, the pyroarsenate  $\text{Mg}_2\text{As}_2\text{O}_7$  remains and any mercury salts present are volatilised. This forms the basis of a delicate test for arsenious and arsenic arsenic.

† Mix a drop of the test solution in a micro-crucible with 1–2 drops of concentrated ammonia solution, 2 drops of "20-volume" hydrogen peroxide, and 2 drops of 10 per cent magnesium chloride solution.

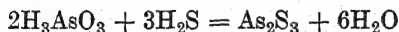
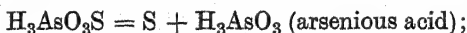
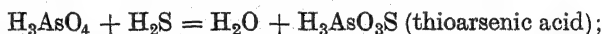
Evaporate slowly and finally heat until fuming ceases. Treat the residue with 1-2 drops of a solution of stannous chloride in concentrated hydrochloric acid, and warm slightly. A brown or black precipitate or coloration is obtained.

Sensitivity: 1  $\mu$ g. As. Concentration limit: 1 in 50,000.

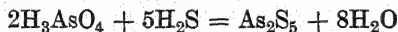
### III, 12. REACTIONS OF ARSENIC COMPOUNDS

Use a solution of sodium arsenate,  $\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O}$  or a solution of arsenic pentoxide  $\text{As}_2\text{O}_5$ , containing some dilute hydrochloric acid.

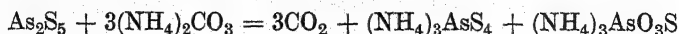
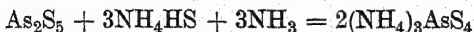
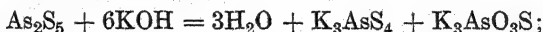
**1. Hydrogen Sulphide:** no immediate precipitate in the presence of dilute hydrochloric acid. If the passage of the gas is continued, a mixture of arsenious sulphide  $\text{As}_2\text{S}_3$  and sulphur is slowly precipitated. Precipitation is more rapid in hot solution.



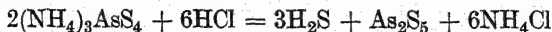
If a large excess of concentrated hydrochloric acid is present and hydrogen sulphide is passed rapidly into the cold solution, yellow arsenic pentasulphide  $\text{As}_2\text{S}_5$  is precipitated; in the hot solution, the precipitate consists of a mixture of the tri- and penta-sulphides.



Arsenic pentasulphide, like the trisulphide, is readily soluble in solutions of caustic alkalis, ammonia, ammonium sulphide or polysulphide and ammonium carbonate, but is insoluble in boiling concentrated hydrochloric acid:

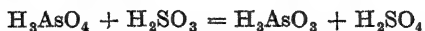


Upon acidifying these solutions with hydrochloric acid, arsenic pentasulphide is precipitated:

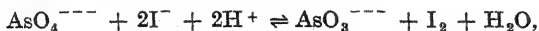


For the rapid precipitation of arsenic from solutions of arsenates without using a large excess of hydrochloric acid, sulphur dioxide may be passed into the slightly acid solution in order to reduce the arsenic to the trivalent state and then the excess of sulphur dioxide is boiled off; upon conducting hydrogen sulphide into the warm

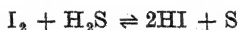
reduced solution, immediate precipitation of arsenic trisulphide occurs:



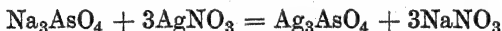
The precipitation can be greatly accelerated by the addition of small amounts of an iodide, say, 1 ml. of a 10 per cent solution, and a little concentrated hydrochloric acid. The iodide acts as a catalyst in that it reduces the arsenic acid thus:



and the iodine liberated is converted into iodide ions by the hydrogen sulphide:



**2. Silver Nitrate Solution:** brownish-red precipitate of silver arsenate  $\text{Ag}_3\text{AsO}_4$  from neutral solutions (distinction from arsenite and phosphate which yield yellow precipitates), soluble in acids and in ammonia solution but insoluble in acetic acid.

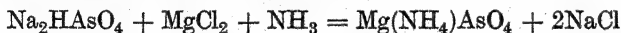


† This reaction may be adapted as a delicate test for arsenic in the following manner. The test is applicable only in the absence of chromates, ferro- and ferri-cyanides, which also give coloured silver salts insoluble in acetic acid.

Place a drop of the test solution in a micro-crucible, add a few drops of concentrated ammonia solution and of "20-volume" hydrogen peroxide, and warm. Acidify with acetic acid and add 2 drops of 1 per cent silver nitrate solution. A brownish-red precipitate or coloration appears.

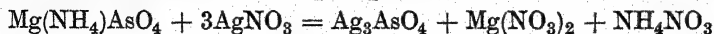
Sensitivity: 6  $\mu\text{g}$ . As. Concentration limit: 1 in 8,000

**3. Magnesia Mixture** (see Section III, 11, reaction 3): white, crystalline precipitate of magnesium ammonium arsenate  $\text{Mg}(\text{NH}_4)\text{AsO}_4 \cdot 6\text{H}_2\text{O}$  from neutral or ammoniacal solution (distinction from arsenite).



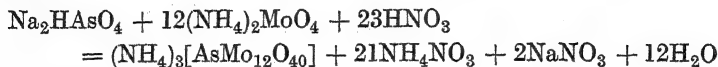
For some purposes (*e.g.* the detection of arsenate in the presence of phosphate), it is better to use the magnesium nitrate reagent (a solution containing  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{NH}_4\text{Cl}$  and a little  $\text{NH}_3$ ).

Upon treating the white precipitate with silver nitrate solution containing a few drops of acetic acid, red silver arsenate is formed (distinction from phosphate):

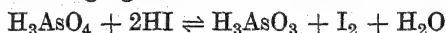


**4. Ammonium Molybdate Solution:** when the reagent and nitric acid are added in considerable excess to a solution of

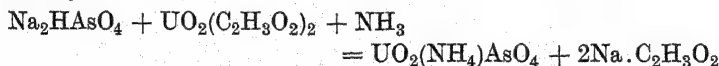
an arsenate, a yellow crystalline precipitate of ammonium arsenomolybdate,  $(\text{NH}_4)_3[\text{AsMo}_{12}\text{O}_{40}]$  is obtained on boiling (distinction from arsenites which give no precipitate, and from phosphates which yield a precipitate in the cold or upon gentle warming). The precipitate is insoluble in nitric acid, but dissolves in ammonia solution and in solutions of caustic alkalis.



**5. Potassium Iodide Solution:** in the presence of concentrated hydrochloric acid, iodine is precipitated; upon shaking the mixture with 1–2 ml. of chloroform or of carbon tetrachloride, the latter is coloured blue by the iodine. The reaction may be used for the *detection of arsenate in the presence of arsenite*; oxidising agents must be absent.



**6. Uranyl Acetate Solution:** light yellow, gelatinous precipitate of uranyl ammonium arsenate  $\text{UO}_2(\text{NH}_4)\text{AsO}_4 \cdot x\text{H}_2\text{O}$  in the presence of excess of ammonium acetate, soluble in mineral acids but insoluble in acetic acid. If precipitation is carried out from a hot solution of an arsenate, the precipitate is obtained in granular form. This test provides an excellent method of distinction from arsenites, which do not give a precipitate with the reagent (an approximately 0.1*N* solution of uranyl acetate).



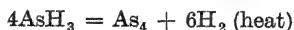
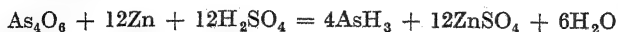
### III, 13. SPECIAL TESTS FOR SMALL AMOUNTS OF ARSENIC

The following tests are applicable to *all* arsenic compounds.

(i) **Marsh's Test.**—This test, which must be carried out in the fume chamber, is based upon the fact that all soluble compounds of arsenic are reduced by "nascent" hydrogen in acid solution to arsine  $\text{AsH}_3$ , a colourless, extremely poisonous gas with a garlic-like odour. If the gas, mixed with hydrogen, be conducted through a heated glass tube, it is decomposed into hydrogen and metallic arsenic, which is deposited as a brownish-black "mirror" just beyond the heated part of the tube.

On igniting the mixed gases, composed of hydrogen and arsine (after all the air has been expelled from the apparatus), they burn with a livid blue flame, and white fumes of arsenious oxide are

evolved; if the inside of a small porcelain dish be pressed down upon the flame, a black deposit of arsenic is obtained on the cool surface, and the deposit is readily soluble in sodium hypochlorite or bleaching powder solution (distinction from antimony).



The Marsh test is best carried out as follows. The apparatus is fitted up as shown in Fig. III, 13, 1. A conical flask of about 125 ml. capacity is fitted with a two-holed rubber stopper carrying a thistle funnel reaching nearly to the bottom of the flask and a 5-7 mm. right-angle tube; the latter is attached by a short piece of

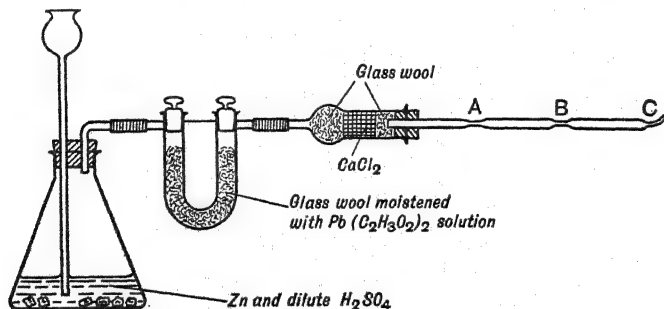


Fig. III, 13, 1

"pressure" tubing to a U-tube filled with glass wool moistened with lead acetate solution to absorb any hydrogen sulphide evolved (this may be dispensed with, if desired, as its efficacy has been questioned), then to a small tube containing anhydrous calcium chloride of about 8 mesh, then to a hard glass tube, *ca.* 25 cm. long and 7 mm. diameter, constricted twice near the middle to about 2 mm. diameter, the distance between the constrictions being 6-8 cm. The drying tubes and the tube ABC are securely supported by means of clamps. All reagents must be arsenic-free. Place 15-20 grams of arsenic-free zinc in the flask, add dilute sulphuric acid (1 : 3) until hydrogen is vigorously evolved. The purity of the reagents is tested by passing the gases, by means of a delivery tube attached by a short piece of rubber tubing to the end of C, through silver nitrate solution for several minutes; the absence of a black precipitate or suspension proves that appreciable quantities of arsenic are not present.



The solution containing the arsenic compound is then added in small amounts at a time to the contents of the flask. If much arsenic is present, there will be an almost immediate blackening of the silver nitrate solution. Disconnect the rubber tube at C. Heat the tube at A to just below the softening point; a mirror of arsenic is deposited in the cooler, less constricted portion of the tube. A second flame may be applied at B to ensure complete decomposition (arsine is extremely poisonous). When a satisfactory mirror has been obtained, remove the flames at A and B and apply a light at C. Hold a cold porcelain dish in the flame, and test the solubility of the black or brownish deposit in sodium hypochlorite solution.

The arsenic in the silver nitrate solution is present as arsenious acid and can be detected by the usual tests, *e.g.* by hydrogen sulphide after removing the excess of silver nitrate with dilute hydrochloric acid, or by neutralising and adding further silver nitrate solution, if necessary.

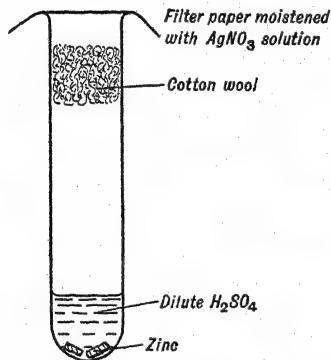


Fig. III, 13, 2

The original Marsh test involved burning and deposition of the arsenic upon a cold surface. Nowadays the mirror test is usually applied. The silver nitrate reaction (sometimes known as Hofmann's test) is very useful as a confirmatory test.

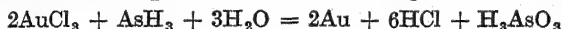
(ii) **Gutzzeit's Test.**—This is essentially a modification of Marsh's test, the chief difference being that only a test-tube is required and the arsine is detected by means of silver nitrate or mercuric chloride. Place 1–2 grams of arsenic-free zinc in a test-tube, add 5–7 ml. of dilute sul-

phuric acid, loosely plug the tube with purified cotton wool and then place a piece of filter paper moistened with 20 per cent silver nitrate solution on top of the tube (Fig. III, 13, 2). It may be necessary to warm the tube gently to produce a regular evolution of hydrogen. At the end of a definite period, say 2 minutes, remove the filter paper and examine the part that covered the test-tube; usually a light-brown spot is obtained owing to the traces of arsenic present in the reagents. Remove the cotton-wool plug, add 1 ml. of the solution to be tested, replace the cotton wool and silver nitrate paper, the latter displaced so that a fresh portion is exposed. After 2 minutes, assuming that the rate of evolution of gas is approximately the same, remove the filter paper and examine the two spots. If much arsenic is present, the second spot (due to metallic silver), will appear black.



Hydrogen sulphide, phosphine  $\text{PH}_3$  and stibine  $\text{SbH}_3$  give a similar reaction. They may be removed by means of a purified cotton-wool plug impregnated with cuprous chloride.

The use of **mercuric chloride paper**, prepared by immersing filter paper in a 5 per cent solution of mercuric chloride in alcohol and drying in the atmosphere out of contact with direct sunlight, constitutes an improvement. This is turned yellow by a little arsine and reddish-brown by larger quantities. Filter paper, impregnated with 1 per cent aqueous solution of "gold chloride"  $\text{HAuCl}_4 \cdot 2\text{H}_2\text{O}$ , may also be employed when a dark-red to blue-red stain is produced. A blank test must be performed with the reagent in all cases.



The test may be performed on the *semimicro scale* with the aid of the apparatus shown in Fig. III, 13, 3. Place 10 drops of the test solution in the semimicro test-tube, add a few granules of arsenic-free zinc and 1 ml. of dilute sulphuric acid. Insert a loose wad of pure cotton wool moistened with lead nitrate solution in the funnel, and on top of this place a disc of drop reaction paper impregnated with 10 per cent silver nitrate solution; the paper may be held in position by a watch glass or microscope slide. Warm the test-tube gently (if necessary) on a water bath to accelerate the reaction, and allow to stand. Examine the silver nitrate paper after about 5 minutes. A grey spot will be obtained; this is occasionally yellow, due to the complex  $\text{Ag}_3\text{As} \cdot 3\text{AgNO}_3$ .

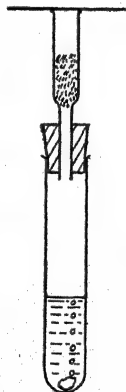


Fig. III, 13, 3

For minute quantities of arsenic, it is convenient to use the apparatus depicted in Fig. II, 6, 13. Mix a drop of the test solution with a few grains of zinc and a few drops of dilute sulphuric acid in the micro test-tube. Insert the funnel with a flat rim, and place a small piece of drop-reaction paper moistened with 20 per cent silver nitrate solution on the flat surface. A grey stain will be obtained.

Sensitivity: 1  $\mu\text{g}$ . As. Concentration limit: 1 in 50,000.

A more sensitive test is provided by drop reaction paper impregnated with gold chloride reagent (a 1 per cent solution of  $\text{HAuCl}_4 \cdot 2\text{H}_2\text{O}$ ). Perform the test as described in the previous paragraph: a blue to blue-red stain of metallic gold is obtained after standing for 10–15 minutes. It is essential to perform a blank test with the reagents to confirm that they are arsenic-free.

Sensitivity: 0.05  $\mu\text{g}$ . As. Concentration limit: 1 in 100,000.

(iii) **Fleitmann's Test.**—This test depends upon the fact that nascent hydrogen generated in alkaline solution, *e.g.* from aluminium or zinc and sodium hydroxide solution, reduces arsenious compounds to arsine, but does not affect antimony compounds. A method of distinguishing arsenic and antimony compounds is thus provided.

Arsenates must first be reduced to the arsenious condition before applying the test. The *modus operandi* is as for the Gutzeit test, except that zinc or aluminium and sodium hydroxide solution replace zinc and dilute sulphuric acid. It is necessary to warm the solutions. A black stain of silver is produced by the action of the arsine.

The apparatus of Fig. III, 13, 3 may be used on the *semimicro scale*. Place 1 ml. of the test solution in the test-tube, add some pure aluminium turnings and 1 ml. of 2*N* potassium hydroxide solution. Gentle warming is usually necessary. A yellow or grey stain is produced after several minutes.

(iv) **Reinsch's Test.**—If a strip of bright copper foil be boiled with a solution of an arsenious compound acidified with at least one-tenth of its bulk of concentrated hydrochloric acid, the arsenic is deposited upon the copper as a grey film of copper arsenide  $\text{Cu}_3\text{As}_2$ . Antimony, mercury, silver and other metals are precipitated under similar conditions. It is therefore necessary to test for arsenic in the deposit in the dry way. The strip is washed with distilled water, dried between filter paper and then gently heated in a test-tube; a white crystalline deposit of arsenious oxide is obtained. The latter is identified by examination with a hand lens, when it will be seen to consist of colourless octahedral and tetrahedral crystals; it may also be dissolved in water and tested for arsenic by Fleitmann's or Bettendorff's test.

Arsenates are also reduced by copper, but only slowly even on boiling.

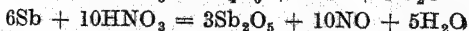
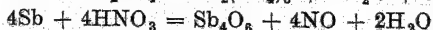
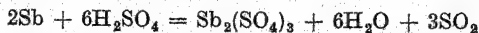
### Dry Tests

(i) *Blowpipe test.*—Arsenic compounds when heated upon charcoal with sodium carbonate give a white incrustation of arsenious oxide, and an odour of garlic is apparent while hot.

(ii) When heated with excess of potassium cyanide and of anhydrous sodium carbonate in a dry bulb tube, a black mirror of arsenic, soluble in sodium hypochlorite solution, is produced in the cooler part of the tube.

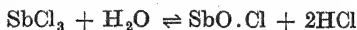
### ANTIMONY, Sb

Antimony is a lustrous, silver-white metal. It is insoluble in hydrochloric acid and in dilute sulphuric acid, is slowly attacked by hot concentrated sulphuric acid yielding unstable antimonious sulphate, and is converted into antimony tri- or pentoxide by nitric acid, depending upon the amount and the concentration of the acid. The best solvent for antimony is aqua regia; a solution of antimony tri- or penta-chloride is formed.

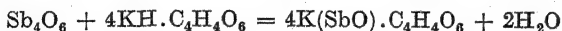




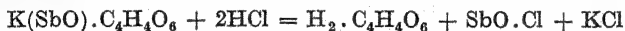
Two series of salts are known, the antimonious and antimonic corresponding respectively to the oxides  $\text{Sb}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_5$ ; the former being the more important. Antimonious compounds react with water similarly to bismuth salts forming compounds containing the antimonyl group  $\text{SbO}-$  (compare Hydrolysis of Salts, Section I, 40).



An important antimonyl compound is tartar emetic, potassium antimonyl tartrate  $\text{K}(\text{SbO}) \cdot \text{C}_4\text{H}_4\text{O}_6 \cdot 0.5\text{H}_2\text{O}$ ; it is prepared by interaction between antimonious oxide and potassium hydrogen tartrate.



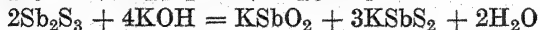
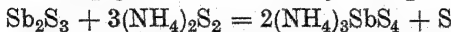
The solubility of antimonyl compounds in solutions of tartaric acid or of tartrates is due to the formation of compounds of this type. The addition of dilute hydrochloric acid to an aqueous solution of tartar emetic gives a white precipitate of antimonyl chloride, soluble in excess of acid:



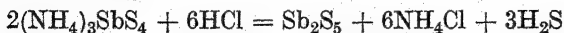
### III, 14. REACTIONS OF ANTIMONIOUS COMPOUNDS

Use a solution of antimony trichloride,  $\text{SbCl}_3$ , prepared by dissolving either the solid trichloride or antimonious oxide,  $\text{Sb}_2\text{O}_3$ , in dilute hydrochloric acid.

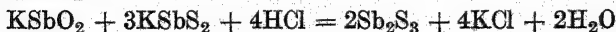
**1. Hydrogen Sulphide:** orange-red precipitate of antimony trisulphide  $\text{Sb}_2\text{S}_3$  from solutions which are not too acid. The precipitate is soluble in warm concentrated hydrochloric acid (distinction and method of separation from arsenious sulphide and mercuric sulphide), in ammonium polysulphide (forming a thioantimonate), and in alkali hydroxide solutions (forming antimonite and thioantimonite).



Upon acidification of the solution of the thioantimonate solution with hydrochloric acid, antimony pentasulphide is precipitated initially but usually decomposes partially into the trisulphide and sulphur:

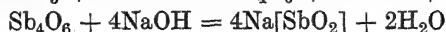


Acidification of the antimonite-thioantimonite mixture leads to the precipitation of the trisulphide:

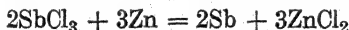


2. **Water**: when the solution is poured into water, a white precipitate of antimonyl chloride  $\text{SbO} \cdot \text{Cl}$  is formed, soluble in hydrochloric acid and in tartaric acid solution (difference from bismuth). With a large excess of water the hydrated oxide  $\text{Sb}_4\text{O}_6 \cdot x\text{H}_2\text{O}$ , is produced.

3. **Sodium Hydroxide or Ammonia Solution**: white precipitate of the hydrated antimonious oxide  $\text{Sb}_4\text{O}_6 \cdot x\text{H}_2\text{O}$ , soluble in concentrated solutions of caustic alkalis forming antimonites.



4. **Zinc**: a black precipitate of antimony is produced. If a little of the antimony trichloride solution is poured upon platinum foil and a fragment of metallic zinc be placed on the foil, a black stain of antimony is formed upon the platinum; the stain (or deposit) should be dissolved in a little warm dilute nitric acid and hydrogen sulphide passed into the solution after dilution; an orange precipitate of antimony trisulphide will be obtained.



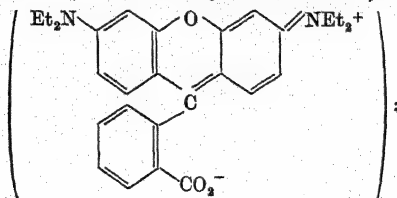
Some stibine  $\text{SbH}_3$  may be evolved when zinc is used; it is preferable to employ tin.

A modification of the above test is to place a drop of the solution containing antimony upon a genuine silver coin and to touch the coin through the drop with a piece of tin or zinc; a black spot will form on the coin.

5. **Iron Wire**: black precipitate of antimony. This may be confirmed as described in reaction 4.

6. **Potassium Iodide Solution**: yellow coloration owing to the formation of a complex salt.

†7. **Rhodamine-B (or Tetraethyl-rhodamine) Reagent**



violet or blue coloration with quinquevalent antimony. Tervalent antimony does not respond to this test, hence it must be oxidised with potassium or sodium nitrite in the presence of strong hydrochloric acid. In Group IIB  $\text{SbCl}_3$  is always formed together with  $\text{SnCl}_4$  when the

precipitate is treated with hydrochloric acid: by oxidising Sb (III) to Sb (V) with a little solid nitrite, an excellent means of testing for Sb in the presence of a large excess of Sn is available. Mercury, gold, thallium, molybdates, vanadates and tungstates in acid solution give similar colour reactions.

The test solution should be strongly acid with hydrochloric acid and the antimonious antimony oxidised by the addition of a little solid sodium or potassium nitrite; a large excess of nitrite should be avoided. Place 1 ml. of the reagent on a spot plate and add 1 drop of the test solution. The bright red colour of the reagent changes to blue.

Sensitivity: 0.5  $\mu$ g. Sb and applicable in the presence of 12,500 times the amount of Sn.

Concentration limit: 1 in 100,000.

The reagent is prepared by dissolving 0.01 g. of rhodamine-B in 100 ml. of water. A more concentrated reagent is obtained by dissolving 0.05 g. of rhodamine-B in a 15 per cent solution of potassium chloride in 2N hydrochloric acid.

†8. **Phosphomolybdic Acid Reagent** ( $H_3[PMo_{12}O_{40}]_{aq.}$ ): "molybdenum blue" is produced by antimonious salts. Of the ions in Group II, only stannous tin interferes with the test. The test solution may consist of the filtered solution obtained by treating the Group IIB precipitate with hydrochloric acid: the antimony is present as  $SbCl_3$  and the tin as  $SnCl_4$ , which has no effect upon the reagent.

Place a drop of the test solution upon drop reaction paper which has been impregnated with the phosphomolybdic acid reagent and hold the paper in steam. A blue coloration appears within a few minutes.

Sensitivity: 0.2  $\mu$ g. Sb. Concentration limit: 1 in 250,000.

Alternatively, place 1 ml. of the test solution in a semimicro test-tube, add 0.5–1 ml. of the reagent, and heat for a short time. The reagent is reduced to a blue compound, which can be extracted with amyl alcohol.

Stannous chloride reduces not only the reactive phosphomolybdic acid but also its relatively unreactive (*e.g.* ammonium or potassium) salts to "molybdenum blue." However, antimonious salts do not reduce ammonium phosphomolybdate:  $Sn^{++}$  may thus be detected in the presence of  $Sb^{+++}$ .

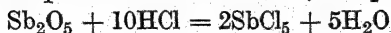
Impregnate drop reaction paper with a solution of phosphomolybdic acid and then hold it for a short time over ammonia gas to form the yellow, sparingly soluble ammonium salt; dry. Place a drop of the test solution on this paper: a blue spot appears if stannous tin is present.

Sensitivity: 0.03  $\mu$ g. Sn. Concentration limit: 1 in 650,000.

The reagent consists of a 5 per cent aqueous solution of phosphomolybdic acid. It does not keep well.

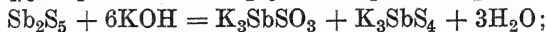
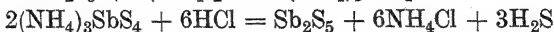
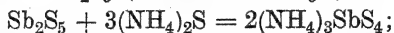
### III, 15. REACTIONS OF ANTIMONIC COMPOUNDS

Use a solution of antimony pentoxide in concentrated hydrochloric acid, or of potassium antimonate,  $KH_2SbO_4$ .



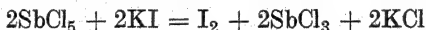
1. **Hydrogen Sulphide:** orange-red precipitate of antimony pentasulphide  $Sb_2S_5$  in moderately acid solutions. The pre-

precipitate is soluble in ammonium sulphide solution (yielding a thio-antimonate), in alkali hydroxide solutions, and is also dissolved by concentrated hydrochloric acid with the formation of antimony trichloride and the separation of sulphur. The thio-salt is decomposed by acids, the pentasulphide being precipitated.



2. **Water:** white precipitate of basic salt.

3. **Potassium Iodide Solution:** iodine separates out from a hydrochloric acid solution (difference from antimonious compounds).



4. **Zinc or Tin:** black precipitate of antimony in the presence of hydrochloric acid (see antimonious compounds). Some stibine ( $\text{SbH}_3$ ) is produced with zinc.

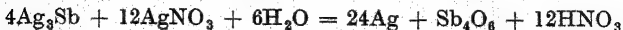
†5. **Rhodamine-B Reagent:** see under Antimonious Compounds.

## SPECIAL TESTS FOR SMALL AMOUNTS OF ANTIMONY

(i) **Marsh's Test.**—This test is carried out exactly as described for arsenic. The stibine  $\text{SbH}_3$  (mixed with hydrogen) which is evolved burns with a faintly bluish-green flame and produces a *dull* black spot upon a cold porcelain dish held in the flame; this deposit is insoluble in sodium hypochlorite or bleaching powder solution, but is dissolved by a solution of tartaric acid (difference from arsenic).

The gas is also decomposed by passage through a tube heated to dull redness. A lustrous mirror of antimony is formed in a similar manner to the arsenic mirror, but it is deposited on *both* sides of the heated portion of the tube because of the greater instability of the stibine. This mirror may be converted into orange-red antimony trisulphide by dissolving it in a little boiling hydrochloric acid and passing hydrogen sulphide into the solution.

When the stibine-hydrogen mixture is passed into a solution of silver nitrate (Hofmann's test), a black precipitate of silver antimonide  $\text{SbAg}_3$  is obtained; this is decomposed by the excess of silver nitrate into silver and antimonious oxide:



It is best to dissolve the precipitate in a solution of tartaric acid and to test for antimony with hydrogen sulphide in the usual manner.

(ii) **Gutzeit's Test.**—A brown stain is produced which is soluble in 80 per cent alcohol, provided the antimony concentration of the solution is not too high.

(iii) **Fleitmann's or Bettendorff's Tests.**—Negative results are obtained when these are applied to antimony compounds (distinction from arsenic).

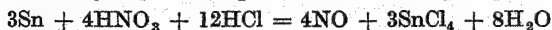
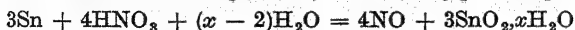
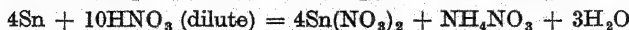
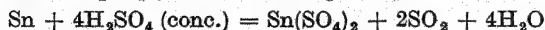
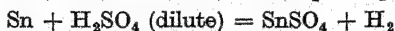
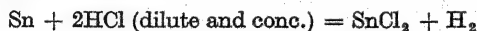
(iv) **Reinsch's Test.**—A grey to black deposit is formed upon the copper. Ignition of this deposit in a dry test-tube gives a non-crystalline sublimate of antimonious oxide, soluble in potassium hydrogen tartrate solution; hydrogen sulphide precipitates orange-red antimony sulphide from this solution, acidified with hydrochloric acid.

## Dry Test

*Blowpipe test.*—When antimony compounds are heated with sodium carbonate upon charcoal, a brittle metallic bead, surrounded by a white incrustation, is obtained.

## TIN, Sn

Tin is a silver-white metal, which is malleable and ductile at ordinary temperatures, but at low temperatures it becomes brittle, due to transformation into an allotropic modification. The metal dissolves slowly in dilute hydrochloric and sulphuric acids with the liberation of hydrogen and the formation of stannous salts; it is readily dissolved by the hot concentrated acids. Dilute nitric acid dissolves tin slowly without any evolution of gas, stannous nitrate and ammonium nitrate being formed; with concentrated nitric acid, a vigorous reaction occurs, a white solid, usually formulated as hydrated stannic oxide  $\text{SnO}_2 \cdot x\text{H}_2\text{O}$  and sometimes known as meta-stannic acid, being produced. Solution takes place readily with aqua regia; stannic chloride is the sole product.

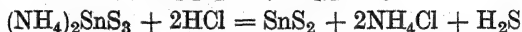
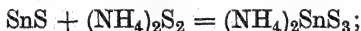
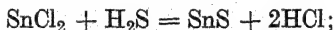


Tin forms two oxides: stannous oxide  $\text{SnO}$  and stannic oxide  $\text{SnO}_2$  from which the stannous and stannic salts respectively may be regarded as derived. Both oxides are amphoteric, the stannic compound to the greater degree.

### III, 16. REACTIONS OF STANNOUS COMPOUNDS

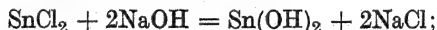
Use a solution of stannous chloride,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , in dilute hydrochloric acid.

**1. Hydrogen Sulphide:** brown precipitate of stannous sulphide  $\text{SnS}$  from not too acid solutions (say in the presence of 0.25–0.3*M* hydrochloric acid or *pH ca.* 0.6 {compare Section I, 37}). The precipitate is soluble in concentrated hydrochloric acid (distinction from arsenious sulphide and mercuric sulphide); it is also soluble in yellow  $\{(\text{NH}_4)_2\text{S}_x\}$ , but not in colourless  $\{\text{NH}_4\text{HS}\}$ , ammonium sulphide solution to form a thioannate. Treatment of the solution of ammonium thioannate with an acid yields a yellow precipitate of *stannic* sulphide  $\text{SnS}_2$ .



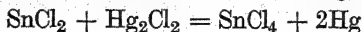
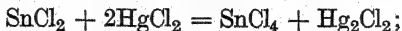
Stannous sulphide is practically insoluble in solutions of caustic alkalis; hence, if potassium hydroxide solution is employed for separating Group IIA and Group IIB, the tin must be oxidised to the stannic state with hydrogen peroxide before precipitation with hydrogen sulphide.

**2. Sodium Hydroxide Solution:** white precipitate of stannous hydroxide, soluble in excess of alkali forming sodium stannite  $\text{Na}_2[\text{SnO}_2]$ .



With ammonia solution, white stannous hydroxide is precipitated, but this is not appreciably soluble in excess of the reagent.

**3. Mercuric Chloride Solution:** white precipitate of mercurous chloride  $\text{Hg}_2\text{Cl}_2$ . If the stannous chloride solution is present in excess, the precipitate turns grey, especially on warming, owing to further reduction to metallic mercury.



**4. Bismuth Nitrate Solution and Sodium Hydroxide Solution:** black precipitate of metallic bismuth (see under Bismuth, Section III, 7, reaction 5).

**5. Metallic Zinc:** spongy tin is deposited which adheres to the zinc. If the zinc rests upon platinum foil, as described

under antimony (Section III, 14, reaction 4), and the solution is weakly acid, the tin is partially deposited upon the zinc in a spongy form but does not stain the platinum. The precipitate should be dissolved in concentrated hydrochloric acid and the mercuric chloride test applied.

†6. **Dimethylglyoxime—Ferric Chloride Test.**\*—No coloration is produced when ferric salts are mixed with the dimethylglyoxime reagent and a little ammonia solution, but if a trace of a ferrous salt is present (produced by reduction with stannous ions), a deep red coloration, due to a ferrous dimethylglyoxime complex, is formed. If tin is present in the Sn (IV) state, it is reduced to Sn (II) by treatment with aluminium or magnesium filings and hydrochloric acid and the solution is filtered. This procedure may be used with the Group IIB precipitate after treatment with hydrochloric acid.

Vanadium, uranyl, titanium, cobalt and nickel ions give a similar reaction; the ions of copper, chromium, manganese, gold, palladium, platinum, selenium and tellurium interfere, as do also molybdates and tungstates: reducing agents, which affect ferric chloride, must be absent.

Place 0.2 ml. of the test solution containing stannous tin (this may consist of the solution obtained from the Group IIB precipitate, reduced with magnesium) in a micro test-tube, acidify (if necessary) with dilute hydrochloric acid, add 0.2 ml. of 0.1N ferric chloride solution, followed by 0.3 ml. of 5 per cent tartaric acid solution (to prevent the formation of ferric hydroxide), 3 drops of the dimethylglyoxime reagent and about 0.5 ml. of 4N ammonia solution. A red coloration is produced.

Sensitivity: 0.05  $\mu$ g. Sn. Concentration limit: 1 in 1,250,000.

The reagent consists of a 1 per cent solution of dimethylglyoxime in ethyl alcohol.

†7. **Cacotheline Reagent** (a nitro-derivative of brucine,  $C_{21}H_{21}O_7N_3$ ): violet coloration with stannous salts. The test solution should be acid (2N HCl), and if tin is in the Sn (IV) state, it should be reduced previously with aluminium or magnesium, and the solution filtered.

The following interfere with the test: strong reducing agents (hydrogen sulphide, dithionites (hyposulphites), sulphites and selenites); V, U, Te, Hg, Bi, Au, Pd, Se, Te, Sb, Mo, W, Co and Ni. The reaction is not selective, but is fairly sensitive: it can be used in the analysis of the Group IIB precipitate. Since ferrous salts have no influence on the test, it may be applied to the tin solution which has been reduced with iron wire.

Impregnate some drop reaction paper with the reagent and, before the paper is quite dry, add a drop of the test solution. A violet spot, surrounded by a less coloured zone, appears on the yellow paper.

Alternatively, treat a little of the test solution in a micro test-tube with a few drops of the reagent. A violet (purple) coloration is produced.

Sensitivity: 0.2  $\mu$ g. Sn. Concentration limit: 1 in 250,000.

The reagent consists of a 0.25 per cent aqueous solution of cacotheline.

\* For formulae, see under Nickel, Section III, 25, reaction 8.

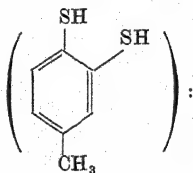
†8. **Diazine Green Reagent** (dyestuff formed by coupling diazotised safranine with dimethyl-aniline).—Stannous chloride reduces the blue diazine green to the red safranine, hence the colour change is blue → violet → red. Titanous chloride reacts similarly, but ferrous salts and similar reducing agents have no effect. The reagent is therefore useful in testing for tin in the mixed sulphides of antimony and tin obtained in routine qualitative analysis. The solution of the sulphides in hydrochloric acid is reduced with iron wire, aluminium or magnesium powder and a drop of the reduced solution employed for the test.

Mix 1 drop of the test solution on a spot plate with 1 ml. of the reagent. The colour changes from blue to violet or red. It is advisable to carry out a blank test.

Sensitivity: 2  $\mu$ g. Sn. Concentration limit: 1 in 25,000.

The reagent consists of a 0.01 per cent aqueous solution of diazine green.

†9. **4-Methyl-1 : 2-dimercapto-benzene** (or "Dithiol") Reagent



red precipitate when warmed with stannous salts in acid solution. The following interfere: silver, lead, mercury, cadmium, arsenic and antimony (yellow precipitates); copper, nickel and cobalt (black precipitates); bismuth (red precipitate); colloidal organic substances (starch, etc.); phosphates and nitrites. The hydrochloric acid concentration of the solution should not exceed 15 per cent.

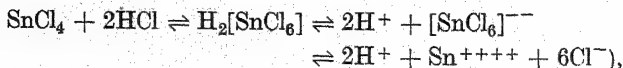
Place 2 drops of the test-solution, acidified with dilute hydrochloric acid, in a micro crucible and add 3 drops of the reagent. Warm (not above 60°C): a red colour or precipitate develops.

Concentration limit: 1 in 500,000.

The reagent is prepared by dissolving 0.2 g. of 4-methyl-1 : 2-dimercapto-benzene in 100 ml. of 1 per cent sodium hydroxide solution and adding 0.3–0.5 g. of thioglycolic acid. The use of the latter in the reagent is not imperative, but it serves to facilitate the reduction of any stannic salt present. The reagent is discarded if a white precipitate of the disulphide forms.

### III, 17. REACTIONS OF STANNIC COMPOUNDS

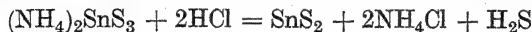
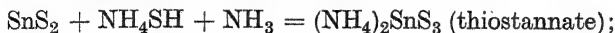
Use a solution of stannic chloride,  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ , in dilute hydrochloric acid (this probably contains hexachlorostannic acid:



or of ammonium stannichloride,  $(\text{NH}_4)_2[\text{SnCl}_6]$ .

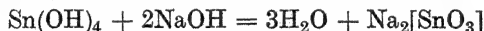


**1. Hydrogen Sulphide:** yellow precipitate of stannic sulphide  $\text{SnS}_2$  from dilute acid solutions ( $>0.3N$ ). The precipitate is soluble in concentrated hydrochloric acid (distinction from arsenious and mercuric sulphides), in solutions of alkali hydroxides, and also in colourless  $(\text{NH}_4\text{HS})$  and yellow  $\{(\text{NH}_4)_2\text{S}_x\}$  ammonium sulphide solutions. Yellow stannic sulphide is precipitated upon acidification.



No precipitation of stannic sulphide in the presence of oxalic acid, due to the formation of the stable complex ion of the type  $[\text{Sn}(\text{C}_2\text{O}_4)_4(\text{H}_2\text{O})_2]^{4-}$ ; this forms the basis of a method of separation of antimony and tin.

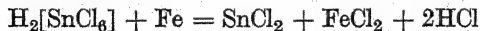
**2. Sodium Hydroxide Solution:** gelatinous white precipitate of stannic hydroxide  $\text{Sn}(\text{OH})_4$ , soluble in excess of the precipitant forming sodium stannate  $\text{Na}_2[\text{SnO}_3]$ .



With ammonia and with sodium carbonate solutions, a similar precipitate is obtained which, however, is insoluble in excess of the reagent.

**3. Mercuric Chloride Solution:** no precipitate (difference from stannous compounds).

**4. Metallic Iron:** reduces stannic salts in hydrochloric acid solution to the stannous condition; filter and test the filtrate with mercuric chloride solution (ferrous salts do not reduce the latter). Similar results are obtained on boiling the solution with copper or antimony.



## Dry Tests

(i) *Blowpipe test.*—All tin compounds when heated with sodium carbonate, preferably in the presence of potassium cyanide, on charcoal give white, malleable and metallic globules of tin which do not mark paper. Part of the metal is oxidised to stannic oxide, especially on strong heating, which forms a white incrustation upon the charcoal.

(ii) *Borax bead test*.—A borax bead which has been coloured pale blue by a trace of copper salt becomes a clear ruby red in the reducing flame if a minute quantity of tin is added.

#### DETECTION AND SEPARATION OF THE METALS IN THE ARSENIC GROUP (GROUP IIB)

The foregoing reactions of the metals of this group provide the facts upon which the following simple table of separation is based. Alternative and more comprehensive schemes are given in Section VII, 12. The student should prepare, or obtain from the teacher, a solid mixture soluble in hydrochloric acid, or a solution containing these elements, and work through the table in order to familiarise himself with it.

The sulphides are precipitated in the presence of hydrochloric acid and then separated from those of Group IIA by warming for a few minutes with yellow ammonium sulphide solution (Table III) or with 2*N* potassium hydroxide solution (Table IIIA), the filtrate being employed for the tests. If no metals of Group IIA are present, the ammonium sulphide or potassium hydroxide treatment is, of course, unnecessary.

### III, 18. Table III. Analysis of the Arsenic Group (Group IIB)

<p>The filtrate from the Copper Group (Group IIA) may contain the thio-salts <math>(\text{NH}_4)_3\text{AsS}_4</math>, <math>(\text{NH}_4)_3\text{SbS}_4</math> and <math>(\text{NH}_4)_2\text{SnS}_3</math>. Dilute with a little water, add dilute HCl in slight excess (<i>i.e.</i> until acid to litmus), warm, filter and wash with a little <math>\text{H}_2\text{S}</math> water. Reject the filtrate. The residue upon the filter may contain <math>\text{As}_2\text{S}_3</math>, <math>\text{As}_4\text{S}_6</math>, <math>\text{Sb}_2\text{S}_3</math>, <math>\text{Sb}_2\text{S}_5</math>, <math>\text{SnS}_2</math> and <math>\text{S}^*</math>. Boil the precipitate gently with 5–10 ml. of concentrated hydrochloric acid, dilute with a little water, and filter.</p>	
<p><b>Residue.</b> May contain <math>\text{As}_2\text{S}_3</math> (and/or <math>\text{As}_4\text{S}_6</math>).</p> <p>Dissolve the ppt. in 3–4 ml. of warm dilute <math>\text{NH}_3</math>, filter (if necessary), add 3–4 ml. of 3% <math>\text{H}_2\text{O}_2</math> and warm to oxidise any arsenite to arsenate. Add a few ml. of the <math>\text{Mg}(\text{NO}_3)_2</math> reagent. Stir and allow to stand.</p> <p>White, crystalline ppt. of <math>\text{Mg}(\text{NH}_4)\text{AsO}_4 \cdot 6\text{H}_2\text{O}</math>.</p> <p><b>As present.</b></p> <p>Confirm as follows: filter off the ppt., and pour 1 ml. of <math>\text{AgNO}_3</math> solution containing a few drops of dilute acetic acid on to the residue on the filter.</p> <p>Brownish-red residue of <math>\text{Ag}_3\text{AsO}_4</math>.</p>	<p><b>Filtrate.</b> May contain <math>\text{H}[\text{SbCl}_4]</math> and <math>\text{H}_2[\text{SnCl}_4]</math>.</p> <p>Divide into two parts:</p> <p><i>First portion.</i>—Make just alkaline with dilute <math>\text{NH}_3</math> solution, add 1–2 g. of oxalic acid, boil and pass <math>\text{H}_2\text{S}</math> for 1 minute.</p> <p>Orange ppt. of <math>\text{Sb}_2\text{S}_3</math>.</p> <p><b>Sb present.</b></p> <p><i>Second portion.</i>—Partially neutralise the liquid, add about 15 cm. of clean iron wire, heat for 5 minutes to reduce the <math>\text{SnCl}_4</math> to <math>\text{SnCl}_2</math>, and filter into a solution of <math>\text{HgCl}_2</math>.</p> <p>White ppt. of <math>\text{Hg}_2\text{Cl}_2</math> or grey ppt. of Hg.</p> <p><b>Sn present.</b></p>

\* If Group IIA absent, commence here.

### III, 18. Table IIIA, Analysis of the Arsenic Group (Group IIB)

The filtrate from the Copper Group (Group IIA) may contain  $\text{KAsO}_2$ ,  $\text{KAsS}_2$ ,  $\text{KSbO}_2$ ,  $\text{KSbS}_2$ ,  $\text{K}_2\text{SnO}_3$  or  $\text{K}_2[\text{Sn}(\text{OH})_6]$ , and  $\text{K}_2\text{SnS}_3$ , and a little  $\text{KHgS}_2$ . Add concentrated  $\text{HCl}$  cautiously (dropwise and with constant stirring) until the solution is distinctly acid to litmus paper. Treat with  $\text{H}_2\text{S}$  for 2–3 minutes to ensure complete precipitation of the sulphides. The formation of a precipitate indicates the possible presence of  $\text{HgS}$ ,  $\text{As}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_3$  and  $\text{SnS}_2$ . Filter, wash the precipitate with a little water, and discard the filtrate and washings.\* Transfer the precipitate to a small conical flask, add 5–10 ml. of concentrated  $\text{HCl}$ , heat to boiling [*FUME CUPBOARD*] and maintain the mixture near the boiling point over a low flame with constant stirring for 5 minutes. Dilute with a little water, and filter.

**Residue.** May contain  $\text{HgS}$  and  $\text{As}_2\text{S}_3$ . If yellow, only  $\text{As}_2\text{S}_3$  present. Wash with water. Pour 5 ml. of dilute  $\text{NH}_3$  through the filter: run filtrate again through filter.

**Residue.** If dark-coloured ( $\text{HgS}$ ).

**Hg present.** Confirm as in Table IIA, if Hg not found in Group IIA.

**Filtrate.** Add dilute  $\text{HNO}_3$  until distinctly acid.

Yellow ppt. of  $\text{As}_2\text{S}_3$ .

**As present.**

Confirm by redissolving in warm aq.  $\text{NH}_3$ , warm for a few minutes with 3%  $\text{H}_2\text{O}_2$  to oxidise arsenite to arsenate, add  $\text{Mg}(\text{NO}_3)_2$  reagent, stir and allow to stand. White ppt. of  $\text{Mg}(\text{NH}_4)\text{AsO}_4 \cdot 6\text{H}_2\text{O}$ . Filter and wash with a little water. Pour on to the filter 1 ml. of  $\text{AgNO}_3$  solution containing a few drops of dilute acetic acid.

Brownish-red residue of  $\text{Ag}_3\text{AsO}_4$ .

**Filtrate.** May contain  $\text{H}[\text{SbCl}_4]$  and  $\text{H}_2[\text{SnCl}_6]$ .

Divide into three parts.

(i) Render just alkaline with aq.  $\text{NH}_3$ , add 1–2 g. of oxalic acid, boil and pass  $\text{H}_2\text{S}$  for ca. 1 minute into the hot solution.

Orange ppt. of  $\text{Sb}_2\text{S}_3$ .

**Sb present.**

(ii) To 2 drops of the solution on a spot plate, add 1 minute crystal of  $\text{NaNO}_2$ , stir and add 2 drops of Rhodamine-B reagent.

Violet coloration or ppt.

**Sb present.**

(iii) Partially neutralise the liquid, add 10–15 cm. of clean iron wire to 1 ml. of the solution, warm gently to reduce tin to the stannous state, and filter into a solution of  $\text{HgCl}_2$ .

White ppt. of  $\text{Hg}_2\text{Cl}_2$  or grey ppt. of Hg.

**Sn present.†**

\* If Group IIA absent, commence here.

† If the proportion of Sb is large, it is better to reduce with Mg turnings or powder and dilute  $\text{HCl}$ .

### III, 18. Table SMIIIA. Analysis of the Arsenic Group (Group IIB)

<p>The centrifugate from the Copper Group (Group IIA) may contain <math>KAsO_2</math>, <math>KAsS_2</math>, <math>KSbO_3</math>, <math>KSbS_2</math>, <math>K_2SnO_3</math> or <math>K_2[Sn(OH)_6]</math>, <math>K_2SnS_3</math> and a little <math>KHgS_2</math>. Transfer to a small conical flask, add concentrated HCl dropwise and with stirring until the mixture is distinctly acid to litmus paper. Treat with <math>H_2S</math> for 30–60 seconds to ensure complete precipitation of the sulphides. The formation of a precipitate indicates the possible presence of <math>HgS</math>, <math>As_2S_3</math>, <math>Sb_2S_3</math> and <math>SnS_2</math>. Centrifuge about 2.5 ml. of the mixture, remove the supernatant liquid with a dropper pipette and discard it. Transfer the remainder of the mixture in the flask to the centrifuge tube, centrifuge, remove the solution and discard it: wash the residue with a little water, completely remove the washings and reject them.* Treat the precipitate with 0.5–1 ml. of concentrated HCl, place in the hot water bath for 2–3 minutes and stir frequently. Centrifuge: remove the centrifugate to a 4 ml. test-tube; wash residue with 0.3 ml. of dilute HCl and add washings to the contents of the test-tube.</p>		
<p><b>Residue.</b> May contain <math>HgS</math> and <math>As_2S_3</math>. If yellow, only <math>As_2S_3</math> present. Wash residue with 5 drops of water: discard washings. Treat residue with 0.5 ml. of dilute aq. <math>NH_3</math>, stir well, and centrifuge.</p>		
<p><b>Residue.</b> If dark-coloured (<math>HgS</math>). <b>Hg present.</b> Confirm as in Table SMIIA, if Hg not found in Copper Group.</p>	<p><b>Centrifugate.</b> Add dilute <math>HNO_3</math> until acid. Yellow ppt. of <math>As_2S_3</math>. <b>As present.</b> Confirm thus: centrifuge and reject washings. Dissolve the ppt. in 0.5 ml. of warm dilute <math>NH_3</math>, add 0.25 ml. of 6% <math>H_2O_2</math> and heat on a water bath for 3 minutes (to oxidise arsenite to arsenate). Add 4 drops of <math>Mg(NO_3)_2</math> reagent and stir. White, crystalline ppt. of <math>Mg(NH_4)AsO_4 \cdot 6H_2O</math>. Centrifuge and reject centrifugate. Add 2 drops of <math>AgNO_3</math> solution and 1 drop of dilute acetic acid. Brownish-red residue of <math>Ag_3AsO_4</math>.</p>	<p><b>Centrifugate.</b> May contain <math>H[SbCl_4]</math> and <math>H_2[SbCl_4]</math>. Divide into two parts. (i) <i>Either</i>—Render just alkaline with concentrated <math>NH_3</math> solution, add 0.3 g. of oxalic acid, and pass <math>H_2S</math> for 20–30 seconds. Orange ppt. of <math>Sb_2S_3</math>. <b>Sb present.</b> <i>Or</i>—To 2 drops of the solution on a spot plate, add a minute crystal of <math>NaNO_2</math>, stir, and add 2 drops of Rhodamine-B reagent. Violet coloration. <b>Sb present.</b> (ii) <i>Either</i>—Introduce 2 cm. of clean iron wire or 20 mg. of iron filings, and heat on a water bath for 3–5 minutes. Centrifuge, and treat the clear centrifugate with 2 drops of <math>HgCl_2</math> solution. White ppt. of <math>Hg_2Cl_2</math> or grey ppt. of Hg. <b>Sn present.†</b> <i>Or</i>—Treat 0.2–0.3 ml. of the solution with 5–10 mg. of Mg powder, add 2 drops of <math>FeCl_3</math> solution, 2–3 drops of 5% tartaric acid solution, 1–2 drops of dimethylglyoxime reagent, and then dil. <math>NH_3</math> solution until basic. Red coloration. <b>Sn present.</b></p>

\* If Group IIA absent, commence here.

† If the proportion of Sb is large, a deposit of Sb is found on the iron wire, which tends to slow down the reduction considerably. It is then better to use Mg turnings or powder for the reduction. Alternatively, the solution (containing Sb and Sn) may be added dropwise to the iron wire reacting in dilute HCl.

*Note.*—With Table SMIII A as a guide, the student should have no difficulty in adapting Table III (Section III, 18) to the semimicro scale.

## THE IRON AND ZINC GROUP (GROUP III)

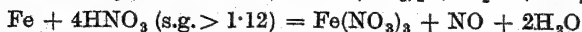
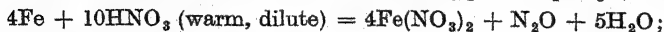
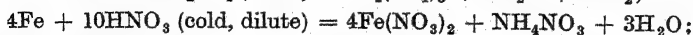
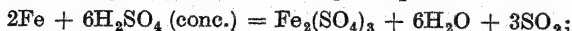
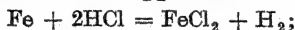
### IRON, ALUMINIUM, CHROMIUM, NICKEL, COBALT, MANGANESE AND ZINC

The metals of this group are not precipitated by the group reagents for Groups I and II, but are all precipitated, in the presence of ammonium chloride, by hydrogen sulphide from their solutions made alkaline with ammonia solution. The metals, with the exception of aluminium and chromium which are precipitated as the hydroxides owing to the complete hydrolysis of the sulphides in aqueous solution, are precipitated as the sulphides. Iron, aluminium and chromium (often accompanied by a little manganese) are also precipitated as the hydroxides by ammonia solution in the presence of ammonium chloride, whilst the other metals of the group remain in solution and may be precipitated as sulphides by hydrogen sulphide. It is therefore usual to subdivide the group into the iron group (iron, aluminium and chromium) or Group IIIA and the zinc group (nickel, cobalt, manganese and zinc) or Group IIIB.

## THE IRON GROUP (GROUP IIIA)

### IRON, Fe

Pure iron is a silver-white, tenacious and ductile metal. The commercial metal is rarely pure and usually contains small quantities of the carbide, silicide, phosphide and sulphide of iron, and a little graphite. Iron dissolves in dilute and concentrated hydrochloric acid and in dilute sulphuric acid with the evolution of hydrogen and the formation of ferrous salts; with hot concentrated sulphuric acid, sulphur dioxide and ferric sulphate are produced. Ferrous and ammonium nitrates are obtained with cold dilute nitric acid, whilst a more concentrated acid yields a ferric salt and either nitrous oxide or nitric oxide depending upon the experimental conditions. Cold concentrated nitric acid renders iron *passive*; in this state it does not react with dilute nitric acid nor does it displace copper from an aqueous solution of a copper salt.

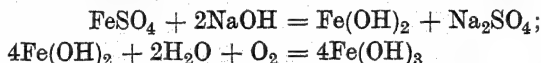


Iron forms two important series of salts: the ferrous salts which may be regarded as derived from ferrous oxide  $\text{FeO}$  in which the metal is divalent, and the ferric salts, which may be regarded as derived from ferric oxide  $\text{Fe}_2\text{O}_3$  and containing trivalent iron.

### III, 19. REACTIONS OF THE FERROUS ION, $\text{Fe}^{++}$

Use a freshly prepared solution of ferrous ammonium sulphate,  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , acidified with a little dilute sulphuric acid. (Solutions of ferrous salts are pale green due to the presence of the  $[\text{Fe}(\text{H}_2\text{O})_6]^{++}$  or  $\text{Fe}^{++}$  ion.)

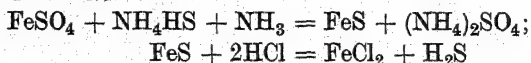
**1. Sodium Hydroxide Solution:** white precipitate of ferrous hydroxide  $\text{Fe}(\text{OH})_2$  in the complete absence of air, insoluble in excess, but soluble in acids. Upon exposure to air, ferrous hydroxide is rapidly oxidised, yielding ultimately reddish-brown ferric hydroxide. Under ordinary conditions it appears as a dirty green precipitate; the addition of hydrogen peroxide immediately oxidises it to ferric hydroxide.



**2. Ammonia Solution:** precipitation of ferrous hydroxide occurs as in reaction 1. In the presence of excess of ammonium chloride solution, the common ion effect (Section I, 14) of the ammonium ions lowers the concentration of the hydroxyl ions to such an extent that the solubility product of ferrous hydroxide  $\text{Fe}(\text{OH})_2$  is not attained and precipitation does not occur. Similar remarks apply to the other divalent elements of Group III, nickel, cobalt, zinc and manganese and also to magnesium.

**3. Hydrogen Sulphide:** no precipitation takes place in acid solution since the sulphide ion concentration,  $[\text{S}^{--}]$ , is insufficient to exceed the solubility product of ferrous sulphide (see Sections I, 15 and I, 16). If the hydrogen ion concentration is reduced, and the sulphide ion concentration correspondingly increased, by the addition of sodium acetate solution, partial precipitation of black ferrous sulphide  $\text{FeS}$  occurs.

**4. Ammonium Sulphide Solution\*:** black precipitate of ferrous sulphide  $\text{FeS}$ , readily soluble in acids with evolution of hydrogen sulphide. The moist precipitate becomes brown upon exposure to air, due to its oxidation to basic ferric sulphate  $\text{Fe}_2\text{O}(\text{SO}_4)_2$ .

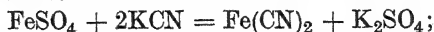


**5. Potassium Cyanide Solution†:** yellowish-brown precipitate of ferrous cyanide  $\text{Fe}(\text{CN})_2$ , soluble in excess of the

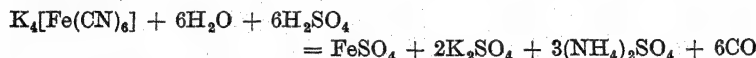
\* Colourless ammonium sulphide should be used for this test: it may be readily prepared by passing  $\text{H}_2\text{S}$  into dilute  $\text{NH}_3$  solution.

† *Very poisonous*; in acid solution the volatile and highly poisonous hydrogen cyanide  $\text{HCN}$  is produced.

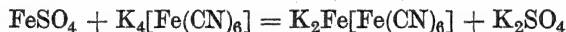
precipitant forming a yellow solution of potassium ferrocyanide  $K_4[Fe(CN)_6]$ .



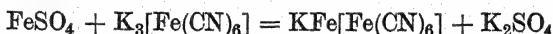
Potassium ferrocyanide is a complex salt, and does not give the typical ferrous ion reactions with ammonium sulphide or sodium hydroxide solutions (compare Section I, 20); the iron present may be detected by first decomposing the compound by boiling with concentrated sulphuric acid (*caution*: poisonous carbon monoxide is evolved).



**6. Potassium Ferrocyanide Solution:** in the complete absence of air, a white precipitate of potassium ferrous ferrocyanide,  $K_2Fe[Fe(CN)_6]$ , is produced. Under ordinary atmospheric conditions a pale blue precipitate is obtained; partial oxidation to potassium ferric ferrocyanide,  $KFe^{III}[Fe^{II}(CN)_6]$ , occurs.



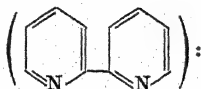
**7. Potassium Ferricyanide Solution:** a dark blue precipitate is produced. This was formerly termed Turnbull's blue and was formulated as potassium ferrous ferricyanide,  $KFe^{II}[Fe^{III}(CN)_6]$ . It is now considered to be identical with Prussian blue, *i.e.* potassium ferric ferrocyanide,  $KFe^{III}[Fe^{II}(CN)_6]$ .



The precipitate is decomposed by sodium or potassium hydroxide solution, ferric hydroxide being precipitated.

**8. Ammonium Thiocyanate Solution:** no coloration is obtained with pure ferrous salts (distinction from ferric salts).

#### †9. $\alpha\alpha'$ -Dipyridyl Reagent



deep red complex bivalent cation  $[Fe(C_5H_4N)_2]^{++}$  with ferrous salts in mineral acid solution. Ferric iron does not react. Other metallic ions react with the reagent in acid solution, but the intensities of the resulting colours are so feeble that they do not interfere with the test for iron provided an excess of the reagent is employed. Large amounts of halides and sulphates reduce the solubility of the ferrous-dipyridyl complex and a red precipitate may be formed.

Treat a drop of the faintly acidified test solution with 1 drop of the reagent on a spot plate: a red coloration is obtained. Alternatively, treat drop-reaction paper (Whatman No. 3 MM., 1st quality) which has been impregnated with the reagent and dried, with a drop of the test solution: a red or pink spot is produced.

Sensitivity:  $0.3 \mu\text{g. Fe}^{++}$ . Concentration limit: 1 in 1,666,000.

If appreciable quantities of ferric salts are present and traces of ferrous salts are sought, it is best to carry out the reaction in a micro crucible lined with paraffin wax and to fix the ferric iron as  $[\text{FeF}_6]^{---}$  by the addition of a few drops of potassium fluoride solution.

The reagent is prepared by dissolving 0.01 g. of  $\alpha\alpha'$ -dipyridyl in 0.5 ml. of alcohol or in 0.5 ml. of 0.1N-hydrochloric acid.

†10. **Dimethylglyoxime Reagent:** soluble red ferrous dimethylglyoxime in ammoniacal solution. Ferric salts give no coloration, but nickel, cobalt and large quantities of copper salts interfere and must be absent. The test may be carried out in the presence of potassium cyanide solution in which nickel dimethylglyoxime (compare Section III, 25) dissolves.

Mix a drop of the test solution with a small crystal of tartaric acid; introduce a drop of the reagent, followed by 2 drops of ammonia solution. A red coloration appears.

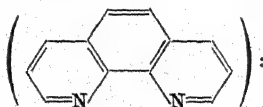
Sensitivity:  $0.04 \mu\text{g. Fe}^{++}$ . Concentration limit: 1 in 125,000.

The coloration fades on standing owing to the oxidation of the ferrous complex.

If it is desired to detect ferric iron by this test, it must first be reduced by a little hydroxylamine hydrochloride.

The reagent consists of a 1 per cent solution of dimethylglyoxime in alcohol.

#### †11. *o*-Phenanthroline Reagent



red coloration, due to the complex cation  $[\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_2)_3]^{++}$  in faintly acid solution. Ferric iron has no effect and must first be reduced to the ferrous state with hydroxylamine hydrochloride if the reagent is to be used in testing for iron.

Place a drop of the faintly acid test solution on a spot plate and add 1 drop of the reagent. A red colour is obtained.

Concentration limit: 1 in 1,500,000.

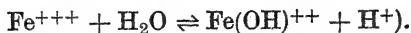
The reagent consists of a 0.1 per cent solution of *o*-phenanthroline in water.

### III, 20. REACTIONS OF THE FERRIC ION, $\text{Fe}^{+++}$

Use a solution of ferric chloride,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ . (All ferric solutions are yellowish-red or yellowish-brown; the ferric ion,  $[\text{Fe}(\text{H}_2\text{O})_6]^{+++}$  or  $\text{Fe}^{+++}$ , is pale violet in colour; hydrolysis

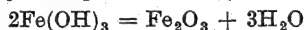
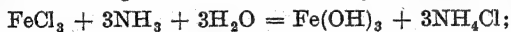


occurs in aqueous solution leading to yellow or brown complexes:



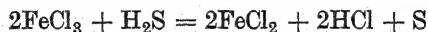
**1. Ammonia Solution:** reddish-brown, gelatinous precipitate of ferric hydroxide  $\text{Fe}(\text{OH})_3$ , insoluble in excess of the reagent, but soluble in acids.

The solubility product of ferric hydroxide is so small ( $1.1 \times 10^{-36}$ ) that complete precipitation takes place even in the presence of ammonium salts (distinction from ferrous iron, nickel, cobalt, manganese, zinc and magnesium). Precipitation does not occur in the presence of certain organic acids (see reaction 8 below). Ferric hydroxide is converted on strong heating into ferric oxide; the ignited oxide is soluble with difficulty in dilute acids, but dissolves on vigorous boiling with concentrated hydrochloric acid.

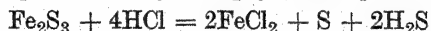


**2. Sodium Hydroxide Solution:** reddish-brown precipitate of ferric hydroxide, insoluble in excess of the reagent (distinction from aluminium and chromium).

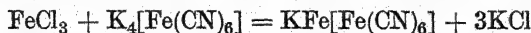
**3. Hydrogen Sulphide:** reduced to ferrous salt in the presence of acid, with separation of sulphur.



**4. Ammonium Sulphide Solution\*:** black precipitate, consisting of ferrous sulphide and sulphur, from acid solutions. From alkaline solutions, a black precipitate of ferric sulphide  $\text{Fe}_2\text{S}_3$  is formed; this is readily soluble in dilute hydrochloric acid forming ferrous chloride and sulphur.



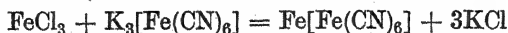
**5. Potassium Ferrocyanide Solution:** intense blue precipitate of potassium ferric ferrocyanide (Prussian blue).



The precipitate is insoluble in dilute hydrochloric acid, but dissolves in oxalic acid solution, in concentrated hydrochloric acid, and also in a large excess of the precipitant with the production of a blue solution. It is decomposed by solutions of caustic alkalis with the formation of ferric hydroxide and a ferrocyanide.

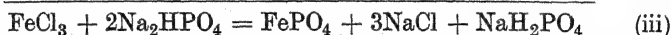
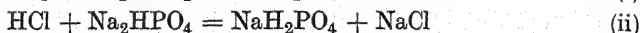
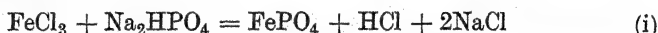
\* Use colourless ammonium sulphide: see Section III, 20, reaction 4.

**6. Potassium Ferricyanide Solution:** a brown coloration is produced, due to ferric ferricyanide  $\text{Fe}[\text{Fe}(\text{CN})_6]$  (distinction from ferrous salts).



Upon adding hydrogen peroxide or a little stannous chloride solution, a blue solution or precipitate (Prussian blue) is obtained: probably the ferricyanide is reduced to ferrocyanide and this then reacts with the ferric iron.

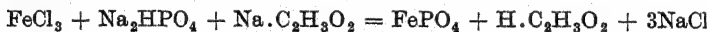
**7. Sodium Phosphate Solution:** yellowish-white precipitate of ferric phosphate  $\text{FePO}_4$ , readily soluble in mineral acids, but insoluble in acetic acid.



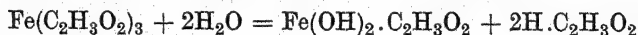
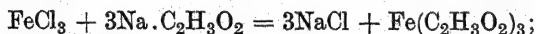
It is evident from the equations that for the complete precipitation of iron as phosphate it is necessary to use excess of the reagent to react with the liberated hydrogen chloride. This is avoided by the addition of excess of sodium acetate solution, since acetic acid is produced {equation (iv)} in which ferric phosphate is insoluble, and precipitation is quantitative.



The net result is:



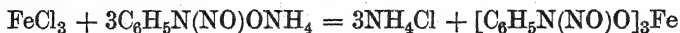
**8. Sodium Acetate Solution:** reddish-brown coloration, attributed variously to ferric acetate  $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_3$  or to the complex ion  $[\text{Fe}(\text{OC}_2\text{H}_3\text{O}_2)_6]^{---}$  or to colloidal ferric hydroxide; upon largely diluting and boiling the solution, the iron is precipitated as basic ferric acetate  $\text{Fe}(\text{OH})_2 \cdot \text{C}_2\text{H}_3\text{O}_2$ .



Reactions 7 and 8 are combined for the removal of the phosphate radical from solutions in which it interferes with the normal course of analysis (see Section VIII, 2); they are also affected by the presence of organic acids (tartaric, citric, sulphosalicylic and malic acids) and by polyhydric alcohols (e.g. glycerol, mannitol, various sugars), and special procedures must be adopted in the ordinary course of analysis when these are present (see Chapter VIII).

**9. Cupferron Reagent** {the ammonium salt of nitroso-phenylhydroxylamine,  $\text{C}_6\text{H}_5\text{N}(\text{NO})\text{ONH}_4$ }: reddish-brown precipitate in the presence of hydrochloric acid. No precipitate is given by the salts of aluminium and chromium under

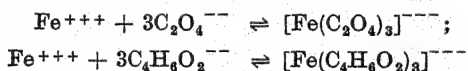
these conditions, *i.e.* in strongly acid solution. The precipitate is soluble in ether, is insoluble in acids, and on treatment with aqueous ammonia solution is converted into ferric hydroxide.



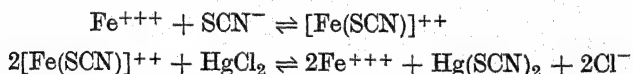
The reagent is prepared by dissolving 2 grams of the solid in 100 ml. of distilled water, but does not keep well. It is recommended that a piece of ammonium carbonate be placed in the stock bottle; this enhances the stability.

**10. Ammonium Thiocyanate Solution:** deep red coloration (difference from ferrous salts). The coloration was formerly attributed to undissociated ferric thiocyanate, but is now known to be due to the ferri-thiocyanate ion,  $[\text{Fe}(\text{SCN})]^{++}$ . The reaction is a reversible one and hence the sensitivity is increased by the addition of excess of the reagent. The ferri-thiocyanate ion is more soluble in ether and in amyl alcohol than in water; accordingly upon shaking with either of these solvents the red colour passes into the organic layer. Phosphates, arsenates, borates, iodates, sulphates, acetates, oxalates, tartrates, citrates and the corresponding free acids interfere with the test.

The organic acids form complex ions of the type :



Fluorides and mercuric chloride bleach the colour because of the formation of the ferrifluoride  $[\text{FeF}_6]^{--}$  ion and the slightly dissociated mercuric thiocyanate  $\text{Hg}(\text{SCN})_2$  respectively.



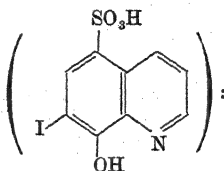
The presence of nitrites should be avoided, for in acid solution they form nitrosyl thiocyanate  $\text{NO}.\text{SCN}$  which yields a red colour, disappearing on heating, similar to that with ferric iron.

† The reaction is well adapted as a spot test and may be carried out as follows. Place a drop of the test solution on a spot plate and add 1 drop of 1 per cent ammonium thiocyanate solution. A deep red coloration appears.

Sensitivity: 0.25  $\mu\text{g}$ .  $\text{Fe}^{+++}$ . Concentration limit: 1 in 200,000.

Coloured salts, *e.g.* those of copper, chromium, cobalt and nickel, reduce the sensitivity of the test.

†11 7-Iodo-8-hydroxyquinoline-5-sulphonic Acid (or Ferron)  
Reagent



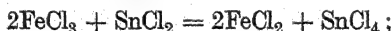
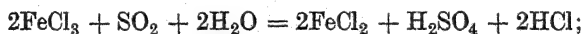
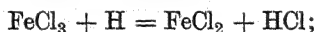
green or greenish-blue coloration with ferric salts in faintly acid solution (pH 2.5-3.0). Ferrous iron does not react: only copper interferes.

Place a few drops of the slightly acid test solution in a micro test-tube and add 1 drop of the reagent. A green coloration appears.

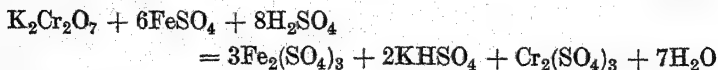
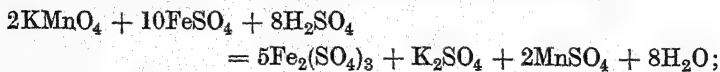
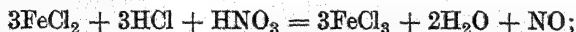
Sensitivity: 0.5  $\mu$ g. Concentration limit: 1 in 1,000,000.

The reagent consists of a 0.2 per cent aqueous solution of 7-iodo-8-hydroxyquinoline-5-sulphonic acid.

**Reduction of ferric to ferrous compounds.**—This may be accomplished by nascent hydrogen (*e.g.* from zinc and dilute hydrochloric or sulphuric acid), hydrogen sulphide, sulphur dioxide, stannous chloride, hydriodic acid, hydroxylamine hydrochloride or hydrazine sulphate.



**Oxidation of ferrous to ferric compounds.**—Oxidation occurs slowly upon exposure to air. Rapid oxidation is effected by concentrated nitric acid, hydrogen peroxide, concentrated hydrochloric acid and potassium chlorate, aqua regia, potassium permanganate, potassium dichromate and ceric sulphate in acid solution.



**Distinctive tests for ferrous and ferric salts.**—These are summarised in the following table. The solution should be slightly acid with hydrochloric acid.

Reagent	Ferrous salt	Ferric salt
Potassium ferrocyanide solution.	White or pale-blue precipitate.	Deep-blue precipitate (Prussian blue).
Potassium ferricyanide solution.	Deep-blue precipitate.	No precipitate; brown coloration.
Ammonium thiocyanate solution.	No coloration in complete absence of ferric salts.	Deep-red coloration, discharged by mercuric chloride solution.
Ammonia solution.	White to greenish-white precipitate.	Reddish-brown precipitate.

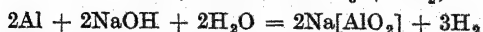
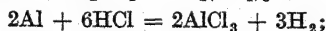
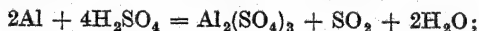
### Dry Tests

(i) *Blowpipe test*.—When iron compounds are heated on charcoal with sodium carbonate, grey metallic particles of iron are produced; these are ordinarily difficult to see, but can be separated from the charcoal by means of a magnet.

(ii) *Borax bead test*.—With a small quantity of iron, the bead is yellowish-brown while hot and yellow when cold in the oxidising flame,\* and pale green in the reducing flame.

### ALUMINIUM, Al

Aluminium is a white, ductile and malleable metal; the powder is grey. The metal is little affected by cold dilute sulphuric acid, but dissolves readily in the hot concentrated acid with the evolution of sulphur dioxide. Nitric acid renders the metal passive; this may be due to the formation of a protective film of oxide. It is readily soluble in hydrochloric acid (dilute and concentrated) with the evolution of hydrogen. Very pure aluminium, however, dissolves slowly in concentrated hydrochloric acid, but solution can be accelerated by adding a little mercuric chloride solution. With caustic alkalis a solution of an aluminate is formed,



Aluminium forms only one series of salts derived from the oxide  $\text{Al}_2\text{O}_3$ .

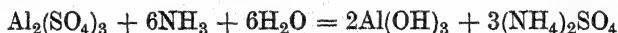
### III, 21. REACTIONS OF THE ALUMINIUM ION, $\text{Al}^{+++}$

Use a solution of aluminium sulphate,  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , or of potash alum,  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ . (All aqueous

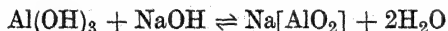
\* With large quantities of iron, the bead is reddish-brown in the oxidising flame.

solutions of aluminium salts are colourless, due to the colourless  $[Al(H_2O)_6]^{+++}$  or  $Al^{+++}$  ion.)

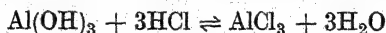
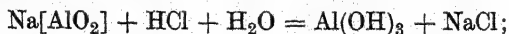
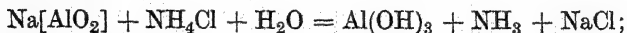
**1. Ammonia Solution:** white gelatinous precipitate of aluminium hydroxide  $Al(OH)_3$ , slightly soluble in excess of the reagent. The solubility is decreased in the presence of ammonium salts owing to the common ion effect (Section I, 14). A small proportion of the precipitate passes into solution as colloidal aluminium hydroxide (aluminium hydroxide *sol*): the *sol* is coagulated on boiling the solution or upon the addition of soluble salts (*e.g.* ammonium chloride) yielding a precipitate of aluminium hydroxide, known as aluminium hydroxide *gel*. To ensure complete precipitation with ammonia solution, the aluminium solution should contain excess of ammonium chloride, the ammonia solution is added in slight excess and the mixture boiled until the liquid has a slight odour of ammonia. When freshly precipitated, it dissolves readily in strong acids and bases, but after boiling it becomes difficultly soluble.



**2. Sodium Hydroxide Solution:** white precipitate of aluminium hydroxide  $Al(OH)_3$ , soluble in excess of the reagent with the formation of sodium aluminate  $Na[AlO_2]$ .

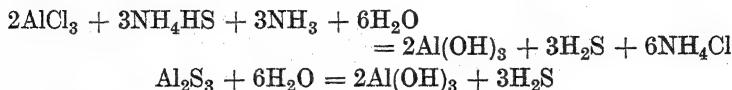


The reaction is a reversible one (compare Section I, 16), and any reagent which will reduce the hydroxyl ion concentration sufficiently should cause the reaction to proceed from right to left with the consequent precipitation of aluminium hydroxide. This may be effected with a solution of ammonium chloride (the hydroxyl ion concentration is reduced owing to the formation of the weak base ammonia, which can be readily removed as ammonia gas on heating) or by the addition of acid; in the latter case a large excess of acid causes the precipitated hydroxide to re-dissolve.

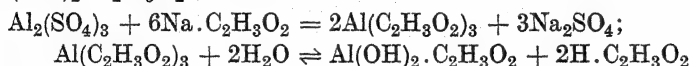


The precipitation of aluminium hydroxide by solutions of sodium hydroxide and ammonia does not take place in the presence of tartaric acid, citric acid, sulphosalicylic acid, malic acid, sugars and other organic hydroxy compounds, due to the formation of soluble complex salts. These organic substances must therefore be decomposed by gentle ignition or by evaporating with concentrated sulphuric or nitric acid before aluminium can be precipitated in the ordinary course of qualitative analysis.

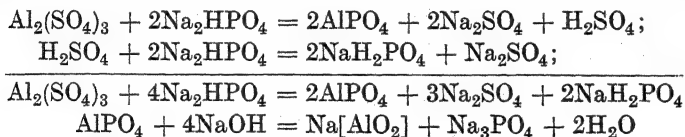
**3. Ammonium Sulphide Solution\*:** white precipitate of aluminium hydroxide. The sulphide of aluminium is completely hydrolysed in the presence of water (compare Section I, 40); it exists only in the dry condition.



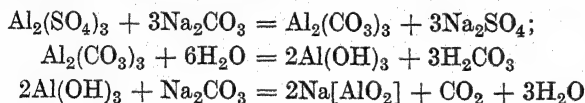
**4. Sodium Acetate Solution:** no precipitate is obtained in cold neutral solutions, but on boiling with excess of the reagent, a voluminous precipitate of basic aluminium acetate  $\text{Al}(\text{OH})_2 \cdot \text{C}_2\text{H}_3\text{O}_2$  is formed.



**5. Sodium Phosphate Solution:** white gelatinous precipitate of aluminium phosphate  $\text{AlPO}_4$ , insoluble in acetic acid, but soluble in mineral acids and in solutions of caustic alkalis.



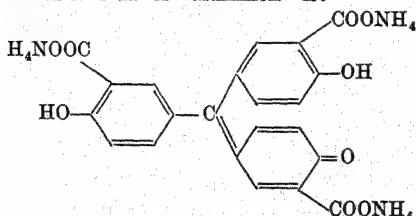
**6. Sodium Carbonate Solution:** white precipitate of aluminium hydroxide, soluble in excess of the precipitant. This is usually attributed to the complete hydrolysis of the initially formed aluminium carbonate, but may be also explained as due to the hydroxyl ions produced by the hydrolysis of the alkali carbonate.



**7. "Aluminon" Reagent** (a solution of the ammonium salt of aurine tricarboxylic acid,  $\text{C}_{22}\text{H}_{14}\text{O}_9$  †): this dyestuff is

\* Use colourless ammonium sulphide: see Section III, 19, Note 4.

† The constitutional formula of "aluminon" is:

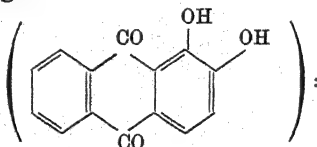


strongly adsorbed by aluminium hydroxide giving a bright red adsorption complex or "lake." The test is applied to the precipitate of aluminium hydroxide obtained in the usual course of analysis, since certain other elements interfere. Dissolve the aluminium hydroxide precipitate in 2 ml. of *M* hydrochloric acid, add 2 ml. of 3*M* ammonium acetate solution and 2 ml. of 0.1 per cent aqueous solution of the reagent. Shake, allow to stand for 5 minutes, and add excess of ammoniacal ammonium carbonate solution to decolourise the excess of the dyestuff and lakes due to traces of chromic hydroxide and silica. A bright red precipitate (or coloration), persisting in the alkaline solution, is obtained.

Iron interferes with the test and should be absent. Chromium forms a similar lake in acetate solution, but this is rapidly decomposed by the addition of the ammoniacal ammonium carbonate solution. Beryllium gives a lake similar to that formed by aluminium. Phosphates, when present in *considerable* quantity, prevent the formation of the lake. It is then best to precipitate the aluminium phosphate by the addition of ammonia solution; the resultant precipitate is redissolved in dilute acid, and the test applied in the usual way.

The reagent is prepared by dissolving 0.25 grams of "aluminon" in 250 ml. of water.

#### †8. Alizarin Reagent



red lake with aluminium hydroxide.

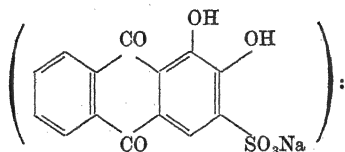
Soak some quantitative filter (or drop-reaction) paper in a saturated alcoholic solution of alizarin and dry it. Place a drop of the acid test solution on the paper and hold it over ammonia fumes until a violet colour (due to ammonium alizarinate) appears. In the presence of large amounts of aluminium, the colour is visible almost immediately. It is best to dry the paper at 100° when the violet colour due to ammonium alizarinate disappears owing to its conversion into ammonia and alizarin: the red colour of the alizarin lake is then clearly visible.

Sensitivity: 0.15  $\mu$ g. Al. Concentration limit: 1 in 333,000.

Iron, chromium, uranium, thorium, titanium and manganese interfere, but this may be obviated by using paper previously treated with potassium ferrocyanide. The ions are thus "fixed" on the paper as insoluble ferrocyanides, and the aluminium solution diffuses beyond as a damp ring. Upon adding a drop of a saturated alcoholic solution of alizarin, exposing to ammonia vapour and drying, a red ring of the alizarin-aluminium lake forms round the precipitate. Uranium ferrocyanide, owing to its slimy nature, has a tendency to spread outwards from the spot and thus obscure the aluminium lake; this difficulty is surmounted by dipping the paper after the alizarin treatment in ammonium carbonate solution which dissolves the uranium ferrocyanide.



## †9. Alizarin-S (or Sodium Alizarin Sulphonate) Reagent



red precipitate or lake in ammoniacal solution, which is fairly stable to dilute acetic acid.

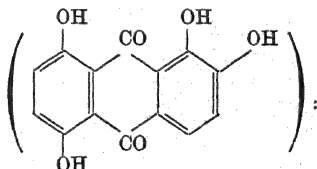
Place a drop of the test solution (which has been treated with just sufficient of *N* sodium hydroxide solution to give the aluminate ion  $[\text{AlO}_2]^-$ ) on a spot plate, add 1 drop of the reagent, then drops of acetic acid until the violet colour just disappears and 1 drop in excess. A red precipitate or coloration appears.

Sensitivity: 0.7  $\mu\text{g}$ . Al. Concentration limit: 1 in 80,000.

A blank test should be made on the sodium hydroxide solution. Salts of Cu, Bi, Fe, Be, Zr, Ti, Co, Ce, rare earths, Zn, Th, U, Ca, Sr and Ba interfere.

The reagent consists of a 0.1 per cent aqueous solution of alizarin-S.

## †10. Quinalizarin (or 1 : 2 : 5 : 8-Tetrahydroxy-anthraquinone) Reagent



red precipitate or coloration under the conditions given below.

Place a drop of the test solution upon the reagent paper; hold it for a short time over a bottle containing concentrated ammonia solution and then over glacial acetic acid until the blue colour (ammonium quinalizarinate) first formed disappears and the unmoistened paper regains the brown colour of free quinalizarin. A red-violet or red spot is formed.

Sensitivity: 0.005  $\mu\text{g}$ . Al (drop of 0.1 ml.).

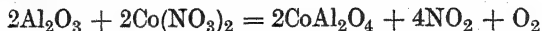
Concentration limit: 1 in 2,000,000.

The reagent paper is prepared by soaking quantitative filter paper in a solution obtained by dissolving 0.01 g. of quinalizarin in 2 ml. of pyridine and then diluting with 20 ml. of acetone.

## Dry Tests

(i) *Blowpipe test*.—Aluminium compounds when heated with sodium carbonate upon charcoal in the blowpipe flame give a white infusible solid, which glows when hot. If the residue be moistened with one or two drops of cobalt nitrate solution and

again heated, a blue infusible mass (Thenard's blue, or cobalt meta-aluminate) is obtained. It is important not to use an excess of cobalt nitrate solution since this yields black cobalt oxide  $\text{Co}_3\text{O}_4$  upon ignition, which masks the colour of the Thenard's blue.



An alternative method for carrying out this test is to soak some ashless filter paper in aluminium salt solution, add a drop or two of cobalt nitrate solution and then to ignite the filter paper in a crucible; the residue is coloured blue.

### CHROMIUM, Cr

Chromium is a white crystalline metal and is not appreciably ductile or malleable. The metal is soluble in hydrochloric acid yielding the blue chromous chloride  $\text{CrCl}_2$  if air is excluded, otherwise chromic chloride  $\text{CrCl}_3$  is formed; hydrogen is evolved. Dilute sulphuric acid reacts similarly forming chromous sulphate  $\text{CrSO}_4$  in the absence of air, and chromic sulphate  $\text{Cr}_2(\text{SO}_4)_3$  in the presence of air. Concentrated sulphuric acid, dilute and concentrated nitric acid induce passivity.

The normal oxide of chromium is the green sesquioxide  $\text{Cr}_2\text{O}_3$ , from which the chromic salts may be regarded as derived. Chromous salts, corresponding to the oxide  $\text{CrO}$ , are extremely readily oxidised in air to chromic salts; the former are rarely encountered in elementary qualitative analysis and will therefore not be considered here. An acidic oxide, chromium trioxide  $\text{CrO}_3$ , forming red deliquescent crystals, is known: this gives rise to the coloured chromates (*e.g.*  $\text{K}_2\text{CrO}_4$  or  $\text{K}_2\text{O}, \text{CrO}_3$ ) and dichromates (*e.g.*  $\text{K}_2\text{Cr}_2\text{O}_7$  or  $\text{K}_2\text{O}, 2\text{CrO}_3$ ), which are discussed in Section IV, 33.

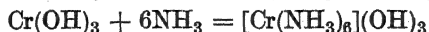
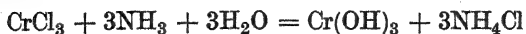
## III, 22. REACTIONS OF THE CHROMIC ION, $\text{Cr}^{+++}$

Use a solution of chromic chloride,  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ , or of chrome alum,  $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ . (Chromic salts are either green or violet in solution.\*)

**1. Ammonia Solution:** grey-green to grey-blue gelatinous precipitate of chromic hydroxide  $\text{Cr}(\text{OH})_3$ , slightly soluble in excess of the precipitant in the cold forming a violet or pink solution containing complex chrome-ammines; upon boiling the solution, chromium hydroxide is precipitated. Hence for complete precipitation of chromium as the hydroxide, it is

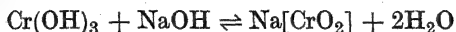
\* Acid solutions, other than chlorides, contain the violet ion  $[\text{Cr}(\text{H}_2\text{O})_6]^{+++}$  or  $\text{Cr}^{+++}$ . Solutions of chromic chloride are green, due to the formation of such complex ions as  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{++}$  and  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ .

essential that the solution be boiling and excess of aqueous ammonia solution be avoided.



In the presence of acetate ions and the absence of other tri-valent metal ions, chromic hydroxide is not precipitated. The precipitation of chromic hydroxide is also prevented by tartrates and by citrates.

**2. Sodium Hydroxide Solution:** precipitate of chromic hydroxide, readily soluble in acids and also in excess of the precipitant in the cold forming a green solution containing sodium chromite  $\text{Na}[\text{CrO}_2]$ . Upon boiling the latter solution, hydrolysis occurs and the chromium is almost quantitatively re-precipitated as the hydroxide (distinction from aluminium).



If hydrogen peroxide is added to the sodium chromite solution, a yellow solution of sodium chromate is produced, which may be identified by the "perchromic acid" reaction (Section IV, 33, reaction 4; reaction 6 below) or by the diphenyl-carbazide reagent (Section IV, 33, reaction 9).



**3. Ammonium Sulphide Solution or Sodium Carbonate Solution:** precipitate of chromic hydroxide. The explanation is similar to that given under Aluminium (Section III, 21, reactions 3 and 6). Chromium sulphide is completely hydrolysed in aqueous solution.

**4. Sodium Acetate Solution:** no precipitate even on boiling the solution.

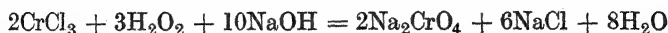
In the presence of considerable amounts of iron and aluminium salts, the precipitate of basic acetates obtained on boiling contains the basic acetate  $\text{Cr}(\text{OH})_2 \cdot \text{C}_2\text{H}_3\text{O}_2$ . If the chromium is present in excess, only a fraction of all the metals will be precipitated as basic acetates, whilst some aluminium, iron and chromium will remain in the filtrate. The basic acetate method of separation (see Section VIII, 2) is therefore uncertain in the presence of a large concentration of chromium.

The precipitation of chromic hydroxide is prevented by the presence of certain organic compounds in solution (see under Aluminium, Section III, 21, reaction 6).

**5. Sodium Phosphate Solution:** green precipitate of chromium phosphate  $\text{CrPO}_4$ , soluble in mineral acids, but practically insoluble in cold dilute acetic acid.

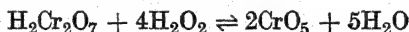


**6. Oxidation to Chromate Test.**—A yellow solution of a chromate is produced by adding excess of sodium hydroxide solution to a solution of a chromic salt, followed by a few ml. of 6 per cent ("20-volume") hydrogen peroxide, and then boiling the resulting mixture for 2–3 minutes. Alternatively, the oxidation may be conducted by adding a little solid sodium perborate  $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$  and boiling for a few minutes.



The chromate is identified:

(a) By adding 2–3 ml. of amyl alcohol, acidifying with dilute sulphuric acid, and then adding a little hydrogen peroxide when it will be found that the organic layer is coloured blue, due to the dissolution of the unstable chromic peroxide (often erroneously called "perchromic acid"). Long usage, however, appears to have established the use of the term "perchromic acid" in the hydrogen peroxide test.

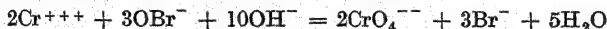


(b) By acidifying with acetic acid and adding barium chloride and sodium acetate solution when a yellow precipitate of barium chromate is formed.

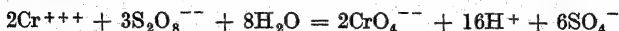
*Note.*—Formerly sodium peroxide was employed to effect the oxidation. The sodium peroxide must be added to the *cold* solution: in hot solution it reacts almost explosively. The use of sodium peroxide is not recommended.

**†7. Test with Diphenylcarbazide Reagent after Conversion into Chromate.**—Chromic chromium may be converted into chromate:

(i) by oxidation with bromine water in the presence of alkali (*i.e.* by hypobromite); the excess of bromine is rendered inactive by the addition of phenol which gives tribromophenol—



(ii) by heating in acid solution with an alkali persulphate in the presence of a trace of a silver salt, which acts as a catalyst in accelerating the oxidation—



Large quantities of halides must be absent as they prevent the catalytic action of the silver ions.

(iii) As detailed in reaction 6.

Solutions of chromates in dilute mineral acids give a soluble violet compound with the diphenylcarbazide reagent.

Place a drop of the test solution in mineral acid on a spot plate, introduce a drop of saturated bromine water followed by 2-3 drops of 2*N*-potassium hydroxide (the solution must be alkaline to litmus). Mix thoroughly, add a crystal of phenol, then a drop of the diphenylcarbazide reagent, and finally 2*N*-sulphuric acid dropwise until the red colour (from the reaction between diphenylcarbazide and alkali) disappears. A blue-violet coloration is obtained.

Sensitivity: 0.25  $\mu\text{g}$ . Cr. Concentration limit: 1 in 2,000,000.

Copper, manganese, nickel and cobalt salts interfere in this procedure because of their precipitation by the alkali.

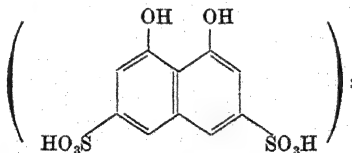
Alternatively, mix a drop of the acidified test solution on a spot plate with a drop of saturated potassium persulphate solution and a drop of 2 per cent silver nitrate solution, and allow to stand for 2-3 minutes. Add a drop of the diphenylcarbazide reagent. A violet or red colour is formed.

Sensitivity: 0.8  $\mu\text{g}$ . Cr. Concentration limit: 1 in 600,000.

Manganese ions interfere (oxidised to permanganic acid) as do also mercuric salts, molybdates and vanadates, which give blue to violet compounds with the reagent in acid solution. The influence of molybdates can be eliminated by the addition of saturated oxalic acid solution thereby forming the complex  $\text{H}_2[\text{MoO}_3(\text{C}_2\text{O}_4)]$ .

The reagent consists of a 1 per cent solution of diphenylcarbazide in alcohol.

#### †8. 1 : 8-Dihydroxynaphthalene-3 : 6-disulphonic Acid (or Chromotropic Acid) Reagent



red coloration (by transmitted light) with an alkali chromate in the presence of nitric acid. Chromic salts may be oxidised with hydrogen peroxide and alkali to chromate, and then acidified with nitric acid before applying the test. The nitric acid serves to eliminate the influence of Fe, U and Ti, which otherwise interfere.

Place a drop of the test solution in a semimicro test-tube, add a drop of the reagent, a drop of dilute nitric acid (1 : 1), and dilute to about 2 ml. Chromates give a red coloration: this is best observed with a white light behind the tube.

The reagent consists of a saturated solution of chromotropic acid in water.

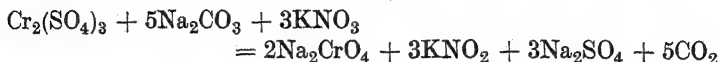
Concentration limit: 1 in 5,000.

#### Dry Tests

(i) *Blowpipe test*.—All chromium compounds when heated with sodium carbonate on charcoal yield a green infusible mass of chromium sesquioxide  $\text{Cr}_2\text{O}_3$ .

(ii) *Borax bead test*.—The bead is coloured green in both the oxidising and reducing flames, but is not very characteristic.

(iii) Fusion with sodium carbonate and potassium nitrate in a loop of platinum wire or upon platinum foil or upon the lid of a nickel crucible results in the formation of a yellow mass of alkali chromate.



#### DETECTION AND SEPARATION OF THE METALS IN THE IRON GROUP (GROUP IIIA)

In the following table it is assumed that the metals of Groups I and II, if present, have been removed as already described, or that only metals of Group IIIA are present; in the former case, it will be necessary to boil off any hydrogen sulphide present (test fumes with lead acetate paper). As in previous instances, the student should make up for himself, or procure from the teacher, a solution containing some or all of the metals of the group. Phosphates, borates, silicates and organic acids are assumed to be absent. For satisfactory precipitation with the group reagent aq.  $\text{NH}_3$  and  $\text{NH}_4\text{Cl}$ , all of the three metals must be present as *trivalent* cations. It is therefore necessary to test the solution for ferrous iron with potassium ferricyanide solution and, if this is present, it must first be oxidised to the ferric state by boiling the solution with a little concentrated nitric acid.

It should be mentioned that manganese (a member of Group IIIB; for reactions, see Section III, 26), when present in the manganous state, should not be precipitated in Group IIIA by excess of  $\text{NH}_3$  solution in the presence of excess of  $\text{NH}_4\text{Cl}$ : in practice, however, the manganous ion is slightly oxidised by exposure of the solution to air and accordingly some manganese may be precipitated as the hydrated dioxide  $\text{MnO}_2 \cdot x\text{H}_2\text{O}$  by the group reagent. For this reason, provision is usually made for the detection of Mn in Group IIIA as well as in Group IIIB.

## III, 23. Table IV. Analysis of the Iron Group (Group IIIA)

\* Add 1-1.5 grams of solid ammonium chloride for each 10 ml. of solution, heat to boiling and add dilute  $\text{NH}_3$  solution slowly until the solution smells of ammonia, boil for 1-2 minutes, filter rapidly and wash with a little 1%  $\text{NH}_4\text{Cl}$  solution.

**Residue.** (T) May contain  $\text{Fe}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{Cr}(\text{OH})_3$  and a little  $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ .† Pierce a hole in the filter paper with a glass rod and wash it into a small evaporating basin or into a small beaker with the aid of about 10 ml. of water. Treat the suspension with about 2 grams of sodium perborate  $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$  (or with excess of  $\text{NaOH}$  solution, followed by 5 ml. of 3%  $\text{H}_2\text{O}_2$  solution). Boil gently until the evolution of  $\text{O}_2$  ceases (2-3 minutes). Filter and wash with a little hot water or 2%  $\text{NH}_4\text{NO}_3$  solution.

**Filtrate.**  
**Reject.**

**Residue.** May contain  $\text{Fe}(\text{OH})_3$  and  $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ .

*Either*—Dissolve a small portion of the ppt. in 1 ml. of dilute  $\text{HNO}_3$  (1 : 1) with the aid, if necessary, of 3-4 drops of 3%  $\text{H}_2\text{O}_2$  or of 1 drop of saturated  $\text{H}_2\text{SO}_4$  solution. Boil (to decompose  $\text{H}_2\text{O}_2$ ), cool thoroughly, add 0.02 gram of  $\text{NaBiO}_3$ , shake and allow the solid to settle.

Violet solution of  $\text{HMnO}_4$ .

**Mn present.**

*Or*—Dissolve a little of the ppt. in 2-3 ml. of dilute  $\text{HNO}_3$  (1 : 1) with the aid of a few drops of 3%  $\text{H}_2\text{O}_2$ , if necessary. Add 0.5 gram of  $\text{PbO}_2$ , boil gently for 2 minutes and allow to settle.

Violet solution of  $\text{HMnO}_4$ .

**Mn present.**

Dissolve another portion of the ppt. in a little dilute  $\text{HCl}$  (filter, if necessary).

*Either*—Add a few drops of  $\text{KSCN}$  solution.

Deep red coloration.

**Fe present.**

*Or*—Add  $\text{K}_4[\text{Fe}(\text{CN})_6]$  solution.

Blue ppt.

**Fe present.**

The original solution or substance should be tested with  $\text{K}_4[\text{Fe}(\text{CN})_6]$  and with  $\text{KSCN}$  to determine whether  $\text{Fe}^{++}$  or  $\text{Fe}^{+++}$ .

**Filtrate.** May contain  $\text{Na}_2\text{CrO}_4$  (yellow) or  $\text{NaAlO}_2$  (colourless). If colourless, Cr is absent and need not be considered further. If the solution is yellow, Cr is indicated.

Divide the liquid into three parts. (Use test (i) or (ii).)

(i) Acidify with acetic acid, and add lead acetate solution.

Yellow ppt. of  $\text{PbCrO}_4$ .

**Cr present.**

(ii) Acidify 2 ml. with dilute  $\text{HNO}_3$ , cool well, add 1 ml. of amyl alcohol, and then 4 drops of 3%  $\text{H}_2\text{O}_2$  solution. Shake well and allow the two layers to separate.

Blue upper layer (containing "perchromic acid"; it does not keep well).

**Cr present.**

(iii) Acidify with dilute  $\text{HCl}$  (test with litmus paper), then add dilute  $\text{NH}_3$  solution until just alkaline. Heat to boiling. Filter.

White gelatinous ppt. of  $\text{Al}(\text{OH})_3$ .

**Al present.**

Confirm Al thus: dissolve a small portion of the ppt. in 1 ml. of dilute  $\text{HCl}$ . Cool, add 1 ml. of 10% ammonium acetate solution and 0.5 ml. of the "aluminon" reagent. Stir the solution and render basic with ammonium carbonate solution. A red ppt. confirms the presence of Al.

\* If a ferrous salt is known to be present, it must first be oxidised to the ferric state by warming with a little  $\text{HNO}_3$ , otherwise the precipitation of iron will be incomplete.

† Small quantities of manganese, if present, are often precipitated at this stage. It is therefore best to provide for the identification of Mn in Group IIIA as well as in Group IIIB.

### III, 23. Table SMIV. Analysis of the Iron Group (Group IIIA)

<p>* Add 0.2 gram of solid <math>\text{NH}_4\text{Cl}</math> (or 1 ml. of 20% <math>\text{NH}_4\text{Cl}</math> solution), followed by dilute <math>\text{NH}_3</math> solution until precipitation seems complete and the solution is ammoniacal, and then add a further 0.5 ml. Warm on a water bath with stirring for 1-2 minutes. Centrifuge.</p>	
<p><b>Residue.</b> (T) Wash with a little dilute aq. <math>\text{NH}_3</math> and reject the washings. The ppt. may contain <math>\text{Fe}(\text{OH})_3</math>, <math>\text{Al}(\text{OH})_3</math>, <math>\text{Cr}(\text{OH})_3</math> and a little <math>\text{MnO}_2 \cdot x\text{H}_2\text{O}</math>. Transfer the ppt. to a semimicro boiling tube with the aid of 2 ml. of <math>\text{NaOH}</math> solution: add 1 ml. of 3% <math>\text{H}_2\text{O}_2</math> solution or ca. 0.2 gram of sodium perborate, <math>\text{NaBO}_3 \cdot 4\text{H}_2\text{O}</math>. Boil gently until the evolution of <math>\text{O}_2</math> ceases (about 1 minute). Transfer the mixture with the aid of a little water to a centrifuge tube. Centrifuge.</p>	<p><b>Centrifugate.</b> Reject.</p>
<p><b>Residue.</b> May contain <math>\text{Fe}(\text{OH})_3</math> and <math>\text{MnO}_2 \cdot x\text{H}_2\text{O}</math>. Wash with a few drops of hot water or 2% <math>\text{NH}_4\text{NO}_3</math> solution and add washings to 4.</p> <p>Dissolve the ppt. in 0.5 ml. of dilute <math>\text{HNO}_3</math> and, if necessary, 2 drops of 3% <math>\text{H}_2\text{O}_2</math> solution or 1 drop of saturated <math>\text{H}_2\text{SO}_3</math> solution. Warm on water bath to decompose excess of <math>\text{H}_2\text{O}_2</math>. Divide the solution into 2 parts.</p> <p>(i) Add 1 drop of <math>\text{K}_4[\text{Fe}(\text{CN})_6]</math> solution.</p> <p>Blue ppt.</p> <p><b>Fe present.</b></p> <p>The original solution or substance should be tested with <math>\text{K}_4[\text{Fe}(\text{CN})_6]</math> or <math>\text{KSCN}</math> to determine whether <math>\text{Fe}^{++}</math> or <math>\text{Fe}^{+++}</math>.</p> <p>(ii) Dilute with 1 ml. of water, cool, add 10 mg. of <math>\text{NaBiO}_3</math>, shake and allow solid to settle.</p> <p>Violet solution of <math>\text{HMnO}_4</math>.</p> <p><b>Mn present.</b></p>	<p><b>Centrifugate (A).</b> May contain <math>\text{NaAlO}_2</math> and <math>\text{Na}_2\text{CrO}_4</math>; the latter is indicated by the yellow colour of the solution. Divide the solution into 2 parts.</p> <p>(i) <i>Either</i>—Acidify with dilute acetic acid and add 1 drop of lead acetate solution.</p> <p>Yellow ppt. of <math>\text{PbCrO}_4</math>.</p> <p><b>Cr present.</b></p> <p><i>Or</i>—Acidify with dilute <math>\text{HNO}_3</math>. Cool: add 0.3-0.5 ml. of amyl alcohol and 2 drops of 3% <math>\text{H}_2\text{O}_2</math> solution. Shake and allow the two layers to separate.</p> <p>Blue coloration of "perchromic acid" in upper layer.</p> <p><b>Cr present.</b></p> <p>The blue colour does not last long as the compound is unstable.</p> <p>(ii) Acidify with dilute <math>\text{HCl}</math> (litmus paper test) and then render just basic with dilute aq. <math>\text{NH}_3</math>, and add 1 drop in excess. Heat on a water bath for 1 minute.</p> <p>White gelatinous ppt. of <math>\text{Al}(\text{OH})_3</math>.</p> <p><b>Al present.</b></p> <p>Confirm Al thus: centrifuge, wash with a few drops of water, dissolve the ppt. in dilute <math>\text{HCl}</math>, add 0.3 ml. of ammonium acetate solution and 1 drop of the "aluminon" reagent. Mix, allow to stand for 30 seconds, and render alkaline with ammoniacal ammonium carbonate solution. A red ppt. confirms Al.</p>

\* If a ferrous salt is known to be present, it must be oxidised first to the ferric state by warming with a few drops of  $\text{HNO}_3$ , otherwise the precipitation of iron will be incomplete.



## THE ZINC GROUP (GROUP IIIB)

## COBALT, Co

Cobalt is a steel-grey, magnetic solid. It dissolves slowly in warm dilute hydrochloric or sulphuric acid, and more rapidly in nitric acid forming cobaltous compounds, which may be regarded as derived from cobaltous oxide  $\text{CoO}$ . Two other oxides exist: cobaltic oxide  $\text{Co}_2\text{O}_3$ , corresponding to the extremely unstable cobaltic compounds, and cobaltous cobaltic oxide  $\text{Co}_3\text{O}_4$ . All the oxides of cobalt dissolve in acids yielding cobaltous salts.

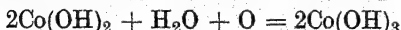
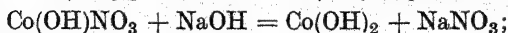
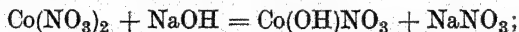


Many stable complex compounds containing trivalent cobalt, *e.g.* potassium cobaltinitrite  $\text{K}_3[\text{Co}(\text{NO}_2)_6]$  and potassium cobalticyanide  $\text{K}_3[\text{Co}(\text{CN})_6]$ , are known.

III, 24. REACTIONS OF THE COBALTOUS ION,  $\text{Co}^{++}$ 

Use a solution of cobalt nitrate,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . (All aqueous solutions of cobaltous salts are pink, due to the presence of the  $[\text{Co}(\text{H}_2\text{O})_6]^{++}$  or  $\text{Co}^{++}$  ion.)

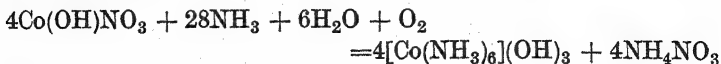
**1. Sodium Hydroxide Solution:** a blue basic salt is precipitated in the cold; upon warming with excess of alkali (sometimes merely upon addition of excess of the reagent), the basic salt is converted into pink cobaltous hydroxide  $\text{Co}(\text{OH})_2$  but a small amount passes into solution. This hydroxide is transformed into the brownish-black cobaltic hydroxide  $\text{Co}(\text{OH})_3$  on exposure to the air, or by prolonged boiling of the aqueous suspension; the change takes place rapidly if an oxidising agent, such as sodium hypochlorite solution or hydrogen peroxide, is added. Cobaltous hydroxide is readily soluble in concentrated solutions of ammonium salts owing to the formation of complex salts; solutions of alkali hydroxides do not, therefore, precipitate cobaltous hydroxide from ammoniacal solution of cobalt salts nor from solutions containing citrates or tartrates.



Cobaltous hydroxide is slightly soluble in a large excess of concentrated sodium hydroxide solution, but cobaltic hydroxide is insoluble.

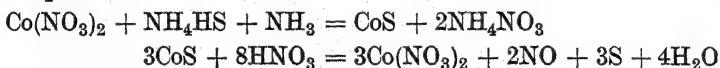
**2. Ammonia Solution:** precipitate of blue basic salt as in reaction 1, readily soluble in excess of the precipitant and in

solutions of ammonium salts. The brownish-yellow ammoniacal solution turns red on exposure to air, more rapidly upon addition of hydrogen peroxide; this is due to the formation of complex salts (cobalt-ammines). These are unaffected by alkali hydroxide solution.



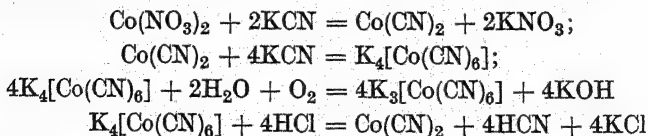
The precipitation of cobaltous hydroxide does not take place in the presence of certain organic acids and organic hydroxy compounds, as in the case of aluminium (Section III, 21, reaction 2).

**3. Ammonium Sulphide Solution\*:** black precipitate of cobalt sulphide  $\text{CoS}$  from neutral or alkaline solutions, insoluble in excess of the reagent, in acetic acid and in very dilute hydrochloric acid (*ca. N*), but is readily soluble in hot concentrated nitric acid and in aqua regia with the separation of sulphur.



**4. Potassium Cyanide Solution:** reddish-brown precipitate of cobaltous cyanide  $\text{Co}(\text{CN})_2$ , soluble in excess of the reagent to form a brown solution containing potassium cobaltocyanide  $\text{K}_4[\text{Co}(\text{CN})_6]$ , analogous to potassium ferrocyanide  $\text{K}_4[\text{Fe}(\text{CN})_6]$ . When the cobaltocyanide solution is treated *in the cold* with dilute hydrochloric acid, cobaltous cyanide is precipitated.

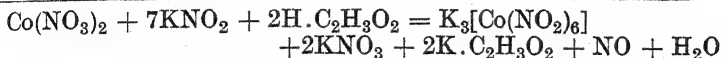
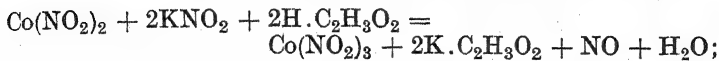
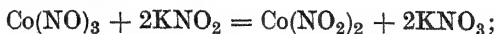
On prolonged boiling of the brown solution, preferably after the addition of a few drops of hydrogen peroxide or of sodium hypochlorite or of sodium hypobromite solution, it assumes a yellow colour, due to oxidation to potassium cobalticyanide  $\text{K}_3[\text{Co}(\text{CN})_6]$ , analogous to potassium ferricyanide  $\text{K}_3[\text{Fe}(\text{CN})_6]$ . The cobalticyanide solution gives no precipitate with acids (distinction from nickel) nor with ammonium sulphide.



**5. Potassium Nitrite Solution:** yellow precipitate of potassium cobaltinitrite  $\text{K}_3[\text{Co}(\text{NO}_2)_6] \cdot 3\text{H}_2\text{O}$  when added in excess to a concentrated solution of a cobalt salt acidified

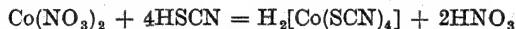
\* Colourless ammonium sulphide solution may be used for this test: it may be readily prepared by passing  $\text{H}_2\text{S}$  into dilute  $\text{NH}_3$  solution.

with acetic acid (distinction from nickel). In dilute solution, the precipitate appears only after standing for several hours, or more rapidly on shaking.



**6. Ammonium Thiocyanate Solution:** a blue solution, due to the cobalti-thiocyanate ion  $[\text{Co}(\text{SCN})_4]^-$ , is produced by adding concentrated  $\text{NH}_4\text{SCN}$  solution (it is best to add a few crystals of the solid salt to the test solution); if amyl alcohol be added and the solution shaken, the blue colour passes into the alcohol layer (distinction from nickel).

The free acid  $\text{H}_2[\text{Co}(\text{SCN})_4]$  is much more soluble in ether and in amyl alcohol than its salts, hence it is best to strongly acidify the solution with concentrated  $\text{HCl}$ : the test is thus rendered much more sensitive.



The disturbing effect of  $\text{Fe}^{+++}$  is overcome by the addition of a fluoride solution, thereby forming the highly stable ferri-fluoride ion  $[\text{FeF}_6]^{---}$ ; alternatively, a little solid  $\text{Na}_2\text{S}_2\text{O}_3$  may be added and the mixture vigorously shaken whereby  $\text{Fe}^{+++}$  is reduced to  $\text{Fe}^{++}$  and  $\text{Na}_2\text{S}_4\text{O}_6$  is produced.

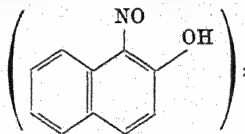
† The reaction may be employed as a spot test as follows. Upon a spot plate, mix 1 drop of the test solution with 5 drops of a saturated solution of ammonium thiocyanate in acetone. A green to blue coloration appears.

Sensitivity: 0.5  $\mu\text{g}$ . Co. Concentration limit: 1 in 100,000.

If iron is present mix 1–2 drops of the slightly acid test solution with a few milligrams of ammonium or sodium fluoride on a spot plate and then add 5 drops of a 10 per cent solution of ammonium thiocyanate in acetone. A blue coloration is produced.

Sensitivity: 1  $\mu\text{g}$ . Co in the presence of 100 times the amount of Fe. Concentration limit: 1 in 50,000.

## 7. $\alpha$ -Nitroso- $\beta$ -naphthol Reagent



reddish-brown precipitate of slightly impure cobalti-nitroso- $\beta$ -naphthol  $\text{Co}(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_3$  (an inner complex salt) in solutions

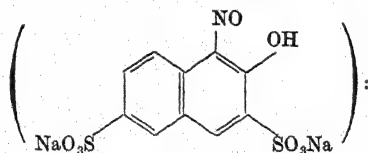
acidified with dilute hydrochloric acid or dilute acetic acid; the precipitate may be extracted by carbon tetrachloride to give a claret-coloured solution. Precipitates are also given by iron ( $\text{Fe}^{++}$  and  $\text{Fe}^{+++}$ ), nickel and uranyl salts in Group III. The nickel complex is soluble in dilute hydrochloric acid; ferric iron is rendered innocuous by the addition of sodium fluoride; the uranyl ion may be removed, as uranyl phosphate, by ammonium phosphate solution. Copper, mercuric mercury, palladium and many other metals interfere. The reaction may, however, be used as a confirmatory test for cobalt in the Group IIIB precipitate after the separation of the manganese and zinc.

The reagent consists of a 1 per cent solution of  $\alpha$ -nitroso- $\beta$ -naphthol in 50 per cent acetic acid, or in ethyl alcohol, or in acetone.

† The technique for using the reaction as a spot test is as follows. Place a drop of the faintly acid test solution on drop reaction paper, and add a drop of the reagent. A brown stain is produced.

Sensitivity 0.05  $\mu\text{g}$ . Co. Concentration limit: 1 in 1,000,000.

### 8. Sodium 1-Nitroso-2-hydroxynaphthalene-3 : 6-di-sulphonate (Nitroso-R-salt) Reagent



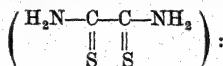
deep red coloration. The test is applicable in the presence of nickel; tin and iron interfere and should be removed; the coloration produced by iron is prevented by the addition of an alkali fluoride.

† Place a drop of the neutral test solution (buffered with sodium acetate) on a spot plate, and add 2-3 drops of the reagent. A red coloration is obtained.

Concentration limit: 1 in 500,000.

The reagent consists of a 1 per cent solution of nitroso-R-salt in water.

### †9. Rubeanic Acid (or Dithio-oxamide) Reagent



yellowish-brown precipitate. Under similar conditions nickel and copper salts give blue and black precipitates respectively (see under

Copper, Section III, 8). Large quantities of ammonium salts reduce the sensitivity.

Place a drop of the test solution upon drop-reaction paper, hold it in ammonia vapour, and then add a drop of the reagent. A brown spot or ring is formed.

Sensitivity: 0.03  $\mu$ g. Co. Concentration limit: 1 in 660,000.

The reagent consists of a 1 per cent solution of rubeanic acid in alcohol.

### Dry Tests

(i) *Blowpipe test*.—All cobalt compounds when ignited with sodium carbonate on charcoal give grey, slightly metallic beads of cobalt. If these are removed, placed upon filter paper and dissolved by the addition of a few drops of dilute nitric acid, a few drops of concentrated hydrochloric acid added and the filter paper dried, the latter is coloured blue by the cobalt chloride produced.

(ii) *Borax bead test*.—This gives a blue bead in both the oxidising and reducing flames. Cobalt meta-borate  $\text{Co}(\text{BO}_2)_2$ , or the complex salt  $\text{Na}_2[\text{Co}(\text{BO}_2)_4]$ , is formed see (Section II, 1). The presence of a large proportion of nickel does not interfere.

### NICKEL, Ni

Nickel is a hard, silver-white metal; it is ductile, malleable and very tenacious. Hydrochloric and sulphuric acids, both dilute and concentrated, attack it slowly; dilute nitric acid dissolves it readily, but the concentrated acid induces passivity.

Only one stable series of salts, the nickelous salts, which may be regarded as derived from the green nickelous oxide  $\text{NiO}$ , is known. A brownish-black nickelic oxide  $\text{Ni}_2\text{O}_3$  exists, but this dissolves in acids forming nickelous compounds.

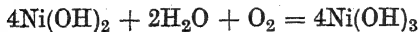
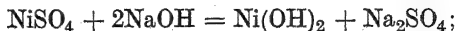


### III, 25. REACTIONS OF THE NICKEL ION, $\text{Ni}^{++}$

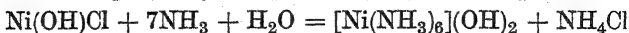
Use a solution of nickel sulphate,  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ , or of nickel chloride,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ . (Solutions of nickelous salts are green, due to the presence of the  $[\text{Ni}(\text{H}_2\text{O})_6]^{++}$  ion; this is usually written as  $\text{Ni}^{++}$ .)

1. **Sodium Hydroxide Solution:** green precipitate of nickelous hydroxide  $\text{Ni}(\text{OH})_2$ , insoluble in excess of the reagent. No precipitation occurs in the presence of tartrate or citrate. The precipitate dissolves in ammonia solution or in solutions of ammonium salts forming greenish-blue solutions of complex nickelous ammine ions (see Section I, 20); these

solutions are not oxidised on boiling with free exposure to air, or upon the addition of hydrogen peroxide (difference from cobalt). Nickelous hydroxide is oxidised by sodium hypochlorite solution to black nickelic hydroxide  $\text{Ni}(\text{OH})_3$ .

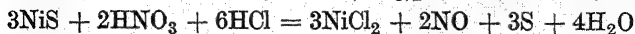
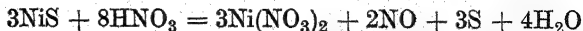


**2. Ammonia Solution:** green precipitate of basic salt, soluble in excess of the reagent forming complex nickel ammine compounds.

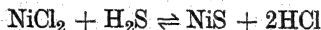


No precipitation takes place with ammonia solution in the presence of ammonium salts; this is because the concentration of hydroxyl ions is so reduced that the solubility product of neither  $\text{Ni}(\text{OH})\text{Cl}$  nor  $\text{Ni}(\text{OH})_2$  is attained (see Sections I, 15 and I, 16).

**3. Ammonium Sulphide Solution\*:** black precipitate of nickel sulphide  $\text{NiS}$  from neutral solutions, slightly soluble in excess of the reagent forming a dark-brown, colloidal solution which runs through the filter paper. If the colloidal solution is boiled or if it is rendered slightly acid with acetic acid and boiled, the colloidal solution (hydrosol) is coagulated and can then be filtered. The presence of large quantities of ammonium chloride usually prevents the formation of the sol. Nickel sulphide is practically insoluble in cold dilute hydrochloric acid, sp. gr. 1.02 (distinction from the sulphides of manganese and zinc) and in acetic acid, but dissolves in hot concentrated nitric acid and in aqua regia with the separation of sulphur.



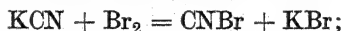
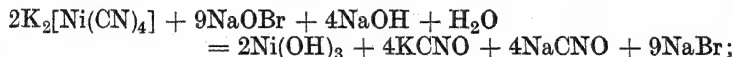
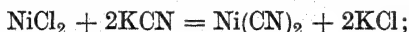
**4. Hydrogen Sulphide:** only part of the nickel is slowly precipitated as nickel sulphide from neutral solutions; no precipitation occurs from solutions containing mineral acid or much acetic acid. Complete precipitation occurs, however, from solutions made alkaline with ammonia solution, or from solutions containing excess of alkali acetate slightly acid with acetic acid (compare Section I, 16).



\* Use colourless ammonium sulphide: see Section III, 24, reaction 2.

**5. Potassium Cyanide Solution:** green precipitate of nickelous cyanide  $\text{Ni}(\text{CN})_2$ , readily soluble in excess of the reagent forming the complex salt, potassium nickelocyanide  $\text{K}_2[\text{Ni}(\text{CN})_4]$  (compare Section I, 20). If this solution be warmed with sodium hypobromite solution (prepared *in situ* by adding bromine water to sodium hydroxide solution), the complex cyanide is decomposed and a black or brown precipitate is formed (difference from cobalt); the precipitate is variously formulated as  $\text{Ni}(\text{OH})_3$  or  $\text{NiO}_2$ . Excess of potassium cyanide solution should be avoided since the bromine water will first react with the excess of cyanide forming cyanogen bromide  $\text{CNBr}$ ; hence it is best to add potassium cyanide solution drop by drop until the initial precipitate is just dissolved.

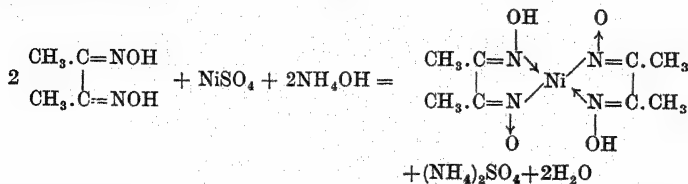
Careful addition of dilute hydrochloric acid to the solution of potassium nickelocyanide precipitates nickel cyanide.



**6. Potassium Nitrite Solution:** no precipitate is produced in the presence of acetic acid (difference from cobalt).

**7.  $\alpha$  - Nitroso -  $\beta$  - naphthol Reagent  $\{\text{C}_{10}\text{H}_6(\text{NO})\text{OH}\}$ :** brown precipitate of composition  $\text{Ni}(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_2$ , soluble in dilute hydrochloric acid (difference from cobalt, which gives a reddish-brown precipitate, insoluble in dilute hydrochloric acid).

**8. Dimethylglyoxime Reagent  $(\text{C}_4\text{H}_8\text{O}_2\text{N}_2)$ :** red precipitate of nickel dimethylglyoxime in solutions just alkaline with ammonia solution or containing sodium acetate.



Ferrous iron (red coloration; compare Section III, 19), bismuth (yellow precipitate), and cobalt when present in large excess (brown

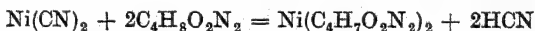
coloration) interfere in ammoniacal solution. The influence of interfering elements ( $\text{Fe}^{++}$  must be oxidised to  $\text{Fe}^{+++}$ , say, by hydrogen peroxide) can be eliminated by the addition of a tartrate. When large quantities of cobalt salts are present, they react with the dimethylglyoxime and a special procedure must be adopted (see below). Oxidising agents must be absent. Palladium, platinum and gold give precipitates in acid solution.

The reagent is prepared by dissolving 1 g. of dimethylglyoxime in 100 ml. of rectified spirit.

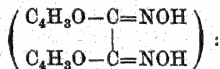
† The spot test technique is as follows. Place a drop of the test solution on drop-reaction paper, add a drop of the above reagent and hold the paper over ammonia vapour. Alternatively, place a drop of the test solution and a drop of the reagent on a spot plate, and add a drop of dilute ammonia solution. A red spot or precipitate (or coloration) is produced.

Sensitivity:  $0.16 \mu\text{g. Ni}$ . Concentration limit: 1 in 300,000.

**Detection of traces of nickel in cobalt salts.** The solution containing the cobalt and nickel is treated with excess of concentrated potassium cyanide solution, followed by "10-volume" hydrogen peroxide whereby the complex cyanides  $\text{K}_3[\text{Co}(\text{CN})_6]$  and  $\text{K}_2[\text{Ni}(\text{CN})_4]$  respectively are formed. Upon adding 40 per cent formaldehyde solution the potassium cobalticyanide is unaffected (and hence remains inactive to dimethylglyoxime) whereas the potassium nickelocyanide is decomposed with the formation of nickel cyanide, which reacts immediately with the dimethylglyoxime.



#### †9. $\alpha$ -Furil-dioxime Reagent



red precipitate in slightly ammoniacal solution.

Place a few drops of the slightly ammoniacal test solution in a micro test-tube and add a few drops of the reagent. A red precipitate or coloration is formed. Alternatively, the reaction may be carried out on a spot plate.

Sensitivity:  $0.02 \mu\text{g. Ni}$ . Concentration limit: 1 in 6,000,000.

The reaction is not disturbed by silver or copper, or by ferric iron, chromium or aluminium in the presence of ammoniacal tartrate solution; if zinc is present, ammonium chloride should first be added; cobaltous ions repress the sensitivity and should be oxidised to the cobaltic state with hydrogen peroxide; ferrous iron interferes and should be oxidised and alkaline tartrate solution added before applying the test.

The reagent consists of a 10 per cent solution of  $\alpha$ -furil-dioxime in alcohol.



†10. **Rubeanic Acid Reagent**  $\{(CS.NH_2)_2\}$ : blue or violet precipitate or coloration in ammoniacal solution. Copper and cobalt, as well as iron, salts interfere with the reaction and should be absent.

Place a drop of the test solution upon drop-reaction paper, hold it over ammonia vapour, and add a drop of the reagent. A blue or blue-violet spot is obtained.

Sensitivity: 0.03  $\mu$ g. Ni. Concentration limit: 1 in 1,250,000.

The **reagent** consists of a 1 per cent solution of rubeanic acid in alcohol.

## Dry Tests

(i) *Blowpipe test*.—All nickel compounds when heated with sodium carbonate on charcoal yield grey, slightly magnetic scales of metallic nickel. If these are placed upon a strip of filter paper, dissolved by means of a few drops of nitric acid, a few drops of concentrated hydrochloric acid added and the filter paper dried by moving it back and forth in the flame or by placing it on the outside of a test-tube containing water which is heated to the boiling point, the paper acquires a green colour owing to the formation of nickelous chloride. On moistening the filter paper with ammonia solution and adding a few drops of the dimethylglyoxime reagent, a red colour is produced.

(ii) *Borax bead test*.—This is coloured brown in the oxidising flame, due to the formation of nickel meta-borate  $Ni(BO_2)_2$  or of the complex meta-borate  $Na_2[Ni(BO_2)_4]$  (see Section II, 1), and grey, due to metallic nickel, in the reducing flame.

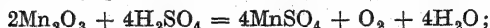
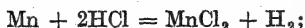
## MANGANESE, Mn

Manganese is a greyish-white metal, similar in appearance to cast iron. It reacts with warm water forming manganous hydroxide and hydrogen. Dilute mineral acids and also acetic acid dissolve it with the production of manganese salts and hydrogen. Sulphur dioxide is evolved with hot concentrated sulphuric acid.

Six oxides of manganese are known:  $MnO$ ,  $Mn_2O_3$ ,  $Mn_3O_4$ ,  $MnO_2$ ,  $MnO_3$  and  $Mn_2O_7$ . The most important compounds, the manganous salts, may be regarded as derived from manganous oxide  $MnO$ ; the manganic salts, related to  $Mn_2O_3$ , which correspond to the ferric salts, are unstable and do not exist under ordinary analytical conditions. All the oxides dissolve in warm hydrochloric acid and hot concentrated sulphuric acid forming manganous salts, the higher oxides being reduced with the evolution of chlorine and oxygen respectively.

The two unstable acidic oxides  $MnO_3$  and  $Mn_2O_7$  are related to the manganates, e.g.  $K_2MnO_4$  or  $K_2O.MnO_3$ , and permanganates,

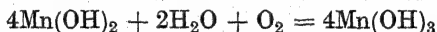
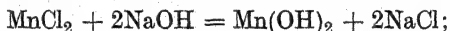
e.g.  $\text{K}_2\text{Mn}_2\text{O}_8$  or  $\text{K}_2\text{O}, \text{Mn}_2\text{O}_7$  respectively. These are discussed in Section IV, 34.



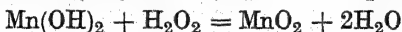
### III, 26. REACTIONS OF THE MANGANOUS ION, $\text{Mn}^{++}$

Use a solution of manganous chloride,  $\text{MnCl}_2, 4\text{H}_2\text{O}$ , or of manganous sulphate,  $\text{MnSO}_4, 5\text{H}_2\text{O}$ . (Manganous compounds are usually pink in aqueous solution, due to the  $[\text{Mn}(\text{H}_2\text{O})_6]^{++}$  or  $\text{Mn}^{++}$  ion.)

**1. Sodium Hydroxide Solution:** white precipitate of manganous hydroxide  $\text{Mn}(\text{OH})_2$ , insoluble in excess of the reagent. The precipitate rapidly oxidises on exposure to air, becoming brown; the brown compound is either manganic hydroxide,  $\text{Mn}(\text{OH})_3$ , or hydrated manganese dioxide  $\text{MnO}_2, x\text{H}_2\text{O}$ .

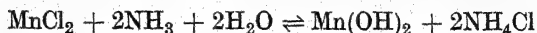


The addition of a little hydrogen peroxide converts the manganous hydroxide rapidly into hydrated manganese dioxide:



**2. Ammonia Solution:** partial precipitation of white manganous hydroxide  $\text{Mn}(\text{OH})_2$ , soluble in solutions of ammonium salts.

No precipitation takes place in the presence of ammonium salts owing to the lowering of the hydroxyl ion concentration and the consequent failure to attain the solubility product of  $\text{Mn}(\text{OH})_2$  (compare Section I, 16). On exposure to air, brown manganic hydroxide or hydrated manganese dioxide is precipitated from the ammoniacal solution. This is important in connexion with the separation from the Group IIIA metals. In precipitating iron, aluminium and chromium, the solution should contain a large excess of ammonium chloride, and be boiled to expel most of the dissolved air, then a slight excess of ammonia solution added and the precipitate filtered *as quickly as possible*. Under these conditions very little manganese will be precipitated.



**3. Ammonium Sulphide Solution\*:** pink (flesh-coloured) precipitate of hydrated manganous sulphide  $\text{MnS}$ , readily

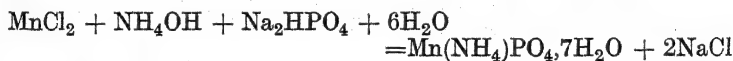
\* Use colourless ammonium sulphide: see Section III, 24, reaction 2.

soluble in dilute acids (distinction from nickel and cobalt) and in acetic acid (distinction from nickel, cobalt and zinc). The presence of ammonium chloride assists precipitation since the sulphide when first formed is colloidal (compare Nickel, Section III, 25, reaction 3). The precipitate turns brown on exposure to air owing to oxidation. Boiling with excess of ammonium sulphide solution converts the pink hydrated form into the less hydrated green sulphide  $3\text{MnS}\cdot\text{H}_2\text{O}$ .

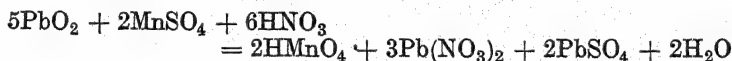


The precipitate dissolves readily in dilute hydrochloric acid (*ca. N*) (distinction from nickel and cobalt).

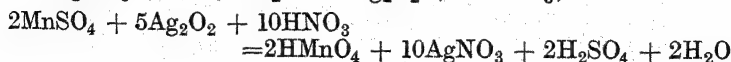
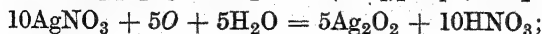
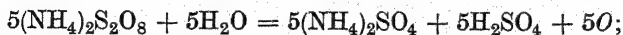
**4. Sodium Phosphate Solution:** flesh-coloured precipitate of manganese ammonium phosphate  $\text{Mn}(\text{NH}_4)\text{PO}_4\cdot 7\text{H}_2\text{O}$  in the presence of excess of ammonia solution.



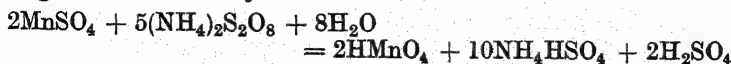
**5. Lead Dioxide and Concentrated Nitric Acid.**—On boiling a dilute solution of a manganous salt, free from hydrochloric acid and chlorides, with lead dioxide (or red lead; which yields the dioxide in the presence of nitric acid) and a little concentrated nitric acid, diluting somewhat and allowing the suspended solid containing unattacked lead dioxide to settle, the supernatant liquid acquires a violet-red (or purple) colour due to permanganic acid. The latter is decomposed by hydrochloric acid hence chlorides should be absent.



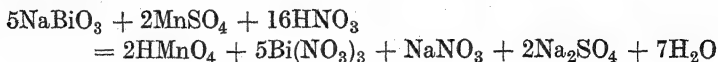
**6. Ammonium or Potassium Persulphate.**—When the solid is boiled with a solution of a manganous salt in dilute sulphuric acid in the presence of a little silver nitrate solution (which acts as a catalyst), a reddish-violet solution of permanganic acid is formed. The unstable silver peroxide is probably intermediately formed and this acts as the oxidising agent.



The gross reaction may be written:



**7. Sodium Bismuthate ( $\text{NaBiO}_3$ ).**—When this solid is added to a *cold* solution of a manganous salt in dilute nitric acid (sp. gr. 1.13) or in dilute sulphuric acid, the mixture stirred and the excess of the reagent filtered off (preferably through asbestos or glass wool or a sintered glass funnel), a solution of permanganic acid is produced.

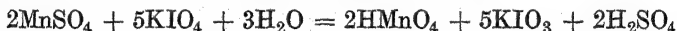


† The spot-test technique is as follows. Place a drop of the test solution on a spot plate, add a drop of concentrated nitric acid and then a little sodium bismuthate. The purple colour of permanganic acid appears. If the solution is so dark that the colour cannot be detected, dilute the mixture with water until the colour appears.

Sensitivity: 25  $\mu\text{g}$  Mn (in 5 ml.). Concentration limit: 1 in 200,000.

**8. Potassium Periodate ( $\text{KIO}_4$ ).**—The manganous sulphate solution is rendered strongly acid with sulphuric or nitric acid or (best) phosphoric acid, 0.2–0.3 gram of potassium periodate added, and the solution boiled for 1 minute. A solution of permanganic acid is formed.

Chlorides must be absent; if present, they must be removed by evaporation with sulphuric or nitric acid before applying the test.

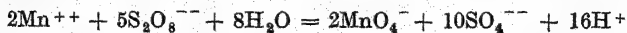


†**9. Potassium Periodate—"Tetrabase" Test.**—A solution of the "tetrabase" (tetramethyl-diamino-diphenylmethane) in chloroform is employed as a sensitive test to identify very small amounts of manganese as permanganic acid. The latter oxidises the "tetrabase" to an intensely blue compound. Chromium salts should be absent for they are oxidised by periodates to chromates, which yield a similar colour with the "tetrabase."

Place a drop of the test solution on a spot plate, followed by a drop of saturated potassium periodate solution and 2 drops of a 1 per cent solution of the "tetrabase" in chloroform. A deep blue colour is formed.

Sensitivity: 0.001  $\mu\text{g}$  Mn. Concentration limit: 1 in 50,000,000.

†**10. Ammonium Persulphate Test.**—Manganese salts in dilute sulphuric or nitric acid solution react only on warming with persulphates with the formation of hydrated manganese dioxide. If, however, the solution contains some silver ions as catalyst, oxidation proceeds to the permanganate state:



Chlorides, bromides, iodides and other salts that precipitate silver should be absent, as should also compounds which will react with permanganic acid.

Place a drop of the test solution in a micro-crucible, add 1 drop of concentrated sulphuric acid and 1 drop of 0.1N-silver nitrate solution,

and stir. Introduce a few milligrams of solid ammonium persulphate and heat *gently*. The characteristic colour of permanganic acid appears.

Sensitivity: 0.1  $\mu\text{g. Mn}$ . Concentration limit: 1 in 500,000.

†11. **Formaldoxime Reagent** ( $\text{HCH} = \text{NOH}$ ): red coloration with alkaline solution of manganous salts. Copper gives a blue-violet coloration, but the interference can be overcome by the use of alkali cyanide. Iron is best removed before applying the test (*e.g.* with a suspension of zinc hydroxide or as the basic acetate), although it may be rendered inactive by the addition of a tartrate. Chromium, cobalt and nickel salts give colorations with the reagent and must therefore be absent.

Place 2 ml. of the test solution, which has been rendered just alkaline with 4*N*-sodium hydroxide, into a semimicro test-tube and add 1 drop of the reagent. A red coloration is obtained.

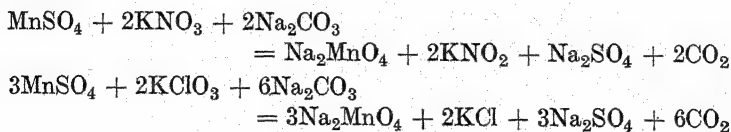
Sensitivity: 0.25  $\mu\text{g.}$  (in 5 ml.). Concentration limit: 1 in 20,000,000.

The reagent consists of a 2.5 per cent solution of formaldoxime in water.

## Dry Tests

(i) *Borax bead test*.—The bead produced in the oxidising flame by small amounts of manganese salts is violet whilst hot and amethyst-red when cold; with larger amounts of manganese the bead is almost brown and may be mistaken for that of nickel. In the reducing flame the manganese bead is colourless whilst that due to nickel is grey.

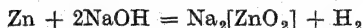
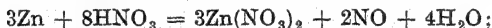
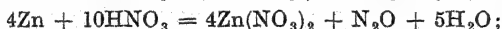
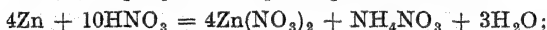
(ii) *Fusion test*.—Fusion of any manganese compound with sodium carbonate and an oxidising agent (potassium chlorate or potassium nitrate) gives a green mass of alkali manganate. The test may be carried out either by heating upon a piece of platinum foil with potassium nitrate and sodium carbonate (if platinum foil is not available, a piece of broken porcelain may be employed), or by fusing a bead of sodium carbonate with a small quantity of the manganese compound in the oxidising flame and dipping the fused mass while hot into a little powdered potassium chlorate or nitrate and reheating (compare Section II, 1).



## ZINC, Zn

Zinc is a bluish-white metal; it is fairly malleable and ductile at 110–150°. The pure metal dissolves very slowly in acids and in alkalis; the presence of impurities, or contact with platinum or

copper, produced by the addition of a few drops of the solutions of the salts of these metals, accelerates the reaction. This explains the solubility of commercial zinc. The latter dissolves readily in dilute hydrochloric and in dilute sulphuric acid, with the evolution of hydrogen. Solution takes place with very dilute nitric acid, but no gas is evolved; with increasing concentration of acid, nitrous oxide or nitric oxide is evolved, depending upon the concentration; concentrated nitric acid has very little action owing to the very slight solubility of zinc nitrate. Sulphur dioxide is evolved with hot concentrated sulphuric acid. Zinc also dissolves in solutions of caustic alkalis with the evolution of hydrogen and the formation of zincates.

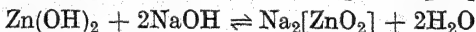
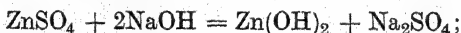


Only one series of salts is known; these may be regarded as derived from the oxide  $\text{ZnO}$ .

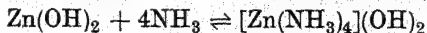
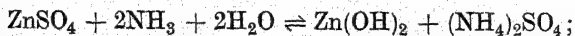
### III, 27. REACTIONS OF THE ZINC ION, $\text{Zn}^{++}$

Use a solution of zinc sulphate,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ . (Zinc compounds are usually colourless in aqueous solution: the ion  $[\text{Zn}(\text{H}_2\text{O})_4]^{++}$  or  $\text{Zn}^{++}$  is colourless.)

**1. Sodium Hydroxide Solution:** white gelatinous precipitate of zinc hydroxide  $\text{Zn}(\text{OH})_2$ , readily soluble in excess of the reagent with the formation of sodium zincate (distinction from manganese). The precipitate also dissolves in dilute acids and is therefore amphoteric.



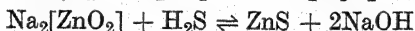
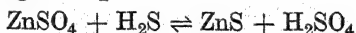
**2. Ammonia Solution:** white precipitate of zinc hydroxide, readily soluble in excess of the reagent and in solutions of ammonium salts owing to the production of complex compounds. The non-precipitation of zinc hydroxide by ammonia solution in the presence of ammonium chloride is due to the lowering of the hydroxyl ion concentration to such a value that the solubility product of  $\text{Zn}(\text{OH})_2$  is not attained (compare Section I, 16).



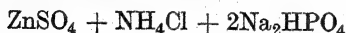
**3. Ammonium Sulphide Solution\*:** white precipitate of zinc sulphide  $\text{ZnS}$  from neutral or alkaline solutions; it is insoluble in excess of the reagent, in acetic acid and in solutions of caustic alkalis, but dissolves in dilute mineral acids. The precipitate thus obtained is partially colloidal; it is difficult to wash and tends to run through the filter paper, particularly on washing. To obtain the zinc sulphide in a form which can be readily filtered, the precipitation is conveniently carried out in boiling solution in the presence of excess of ammonium chloride, and the precipitate washed with dilute ammonium chloride solution containing a little ammonium sulphide.



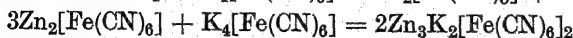
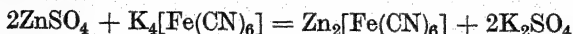
**4. Hydrogen Sulphide:** partial precipitation of zinc sulphide in neutral solutions; when the concentration of acid produced is about  $0.3M$  ( $pH$  about  $0.6$ ), the sulphide ion concentration derived from the hydrogen sulphide is depressed so much by the hydrogen ion concentration from the acid that it is too low to exceed the solubility product of  $\text{ZnS}$ , and consequently precipitation ceases. Upon the addition of alkali acetate to the solution, the hydrogen ion concentration is reduced because of the formation of the feebly dissociated acetic acid, the sulphide ion concentration is correspondingly increased, and precipitation is almost complete (compare Section I, 16). Zinc sulphide is precipitated from solutions of alkali zincates by hydrogen sulphide.



**5. Sodium Phosphate Solution:** white precipitate of zinc ammonium phosphate  $\text{Zn}(\text{NH}_4)\text{PO}_4$  in the presence of ammonium chloride; the precipitate is soluble in ammonia solution and in dilute acids.

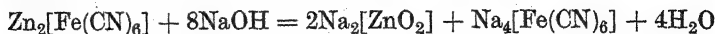


**6. Potassium Ferrocyanide Solution:** white precipitate of zinc ferrocyanide  $\text{Zn}_2[\text{Fe}(\text{CN})_6]$ , which is converted by excess of the reagent into the less soluble zinc potassium ferrocyanide  $\text{Zn}_3\text{K}_2[\text{Fe}(\text{CN})_6]_2$ .



\* Use colourless ammonium sulphide: see Section III, 24, reaction 2.

The precipitate is insoluble in dilute acids, but dissolves in solutions of caustic alkalis:

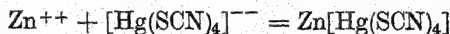


**7. Quinaldinic Acid Reagent** (Quinoline- $\alpha$ -carboxylic acid,  $\text{C}_9\text{H}_6\text{N} \cdot \text{CO}_2\text{H}$ ).—Upon the addition of a few drops of the reagent to a solution of a zinc salt which is faintly acid with acetic acid, a white precipitate of the zinc complex salt  $\text{Zn}(\text{C}_{10}\text{H}_6\text{NO}_2)_2 \cdot \text{H}_2\text{O}$  is obtained. The precipitate is soluble in ammonia solution and in mineral acids, but is reprecipitated on neutralisation. Copper, cadmium, uranium, iron and chromium ions give precipitates with the reagent and should be absent. Cobalt, nickel and manganese ions have no effect. This is an extremely sensitive test for zinc ions, and is a useful confirmatory test for zinc isolated from the Group IIIB separation. The reagent is, however, expensive. The reaction is best carried out on the semimicro scale or as a spot test.

The reagent is prepared by neutralising 1 gram of quinaldinic acid with sodium hydroxide solution and diluting to 100 ml.

**8. Ammonium Mercuri-thiocyanate-Copper Sulphate Test.**—The faintly acid (sulphuric acid or acetic acid) solution is treated with 0.5 ml. of 0.1 per cent copper sulphate solution, followed by 2 ml. of the ammonium mercuri-thiocyanate reagent. A violet precipitate is obtained. The test is rendered still more sensitive by boiling the mixture for 1 minute, cooling and shaking with a little amyl alcohol: the violet precipitate collects at the interface. Iron salts produce a red coloration; this disappears when a little alkali fluoride is added.

Copper salts alone do not give a precipitate with the ammonium mercuri-thiocyanate reagent, whilst zinc ions, if present alone, form a white precipitate of zinc mercuri-thiocyanate:



In the presence of copper ions, the copper complex coprecipitates with that of zinc, and the violet (or blackish-purple) precipitate consists of mixed crystals of  $\text{Zn}[\text{Hg}(\text{SCN})_4] + \text{Cu}[\text{Hg}(\text{SCN})_4]$ .

The ammonium mercuri-thiocyanate reagent is prepared by dissolving 8 grams of mercuric chloride and 9 grams of ammonium thiocyanate in 100 ml. of water.

† Place a drop or two of the test solution, which is slightly acid (preferably with sulphuric acid), on a spot plate, add 1 drop of 0.1 per



cent copper sulphate solution and 1 drop of the ammonium mercuri-thiocyanate reagent. A violet (or blackish-purple) precipitate appears.

The reaction may also be conducted in a semimicro test-tube: here 0.3–0.5 ml. of amyl alcohol is added. The violet precipitate collects at the interface.

Concentration limit: 1 in 10,000.

**9. Ammonium Mercuri-thiocyanate-Cobalt Sulphate Test.**—This test is similar to that described under 8, except that a minute amount of a dilute solution of a cobalt salt (sulphate, acetate or nitrate) is added. Coprecipitation of the cobalt mercuri-thiocyanate gives a blue precipitate composed of mixed crystals of  $\text{Zn}[\text{Hg}(\text{SCN})_4] + \text{Co}[\text{Hg}(\text{SCN})_4]$ . Ferric salts give a red coloration (due to the ferri-thiocyanate ion  $[\text{Fe}(\text{SCN})]^{++}$ ) but this can be eliminated by the addition of a little alkali fluoride (colourless  $[\text{FeF}_6]^{---}$  ions are formed). Copper salts should be absent.

† Place a drop of the test solution (which should be slightly acid, preferably with dilute sulphuric acid), a drop of 0.02 per cent cobalt sulphate solution, and a drop of the ammonium mercuri-thiocyanate reagent on a spot plate or in a micro crucible. A blue precipitate is formed.

The reaction may also be carried out in a semimicro test-tube in the presence of 0.3–0.5 ml. of amyl alcohol.

Sensitivity: 0.2–0.5  $\mu\text{g}$ . Zn. Concentration limit: 1 in 100,000.

**†10. Potassium Ferricyanide-*p*-Phenetidine Test.**—Potassium ferri-cyanide oxidises *p*-phenetidine (4-ethoxyaniline) and other aromatic amines slowly with change of colour and the formation of potassium ferrocyanide. If the ferrocyanide formed is removed by zinc ions as the sparingly soluble, white zinc ferrocyanide, the oxidation proceeds rapidly: the white zinc ferrocyanide is deeply coloured by the adsorption of the coloured oxidation products.

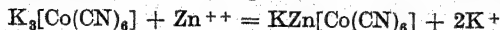
Prepare the reagent by mixing 6 drops of 2 per cent potassium ferri-cyanide solution, 2 drops of *N* sulphuric acid, and 6 drops of 2 per cent *p*-phenetidine hydrochloride solution.

To 0.1 ml. of the freshly-prepared reagent on a spot plate, add a drop of the test solution. A purple to blue coloration or precipitate appears in the presence of zinc. A blank test is desirable.

Sensitivity: 1  $\mu\text{g}$ . Zn. Concentration limit: 1 in 100,000.

The test is especially useful in the presence of Cr, Al and Mg: cations ( $\text{Cu}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Ni}^{++}$ ,  $\text{Fe}^{++}$ , etc.) which give coloured precipitates with potassium ferrocyanide should be absent.

**†11. Rinmann's Green Test.**—The test depends upon the production of Rinmann's green (largely cobalt zincate  $\text{CoZnO}_2$ ) by heating the salts or oxides of zinc and cobalt. An excess of cobaltous oxide must be avoided for it leads to a red-brown coloration: oxidation to cobaltic oxide produces a darkening of colour. Optimum experimental conditions are obtained by converting the zinc into the cobalticyanide:



Ignition of the latter leads to zinc oxide and cobaltous oxide in the correct proportion for the formation of cobalt zincate, whilst carbon from the filter paper (see below) prevents the formation of cobaltic oxide. All other metals must be removed.

Place a few drops of the neutral (litmus) test solution upon potassium cobaltcyanide (Rinmann's green) test paper. Dry the paper over a flame and ignite in a small crucible. Observe the colour of the ash against a white background: part of it will be green.

Sensitivity: 0.6  $\mu$ g. Zn. Concentration limit: 1 in 3,000.

The **potassium cobaltcyanide test paper** is prepared by soaking drop reaction paper or quantitative filter paper in a solution containing 4 grams of potassium cobaltcyanide and 1 gram of potassium chlorate in 100 ml. of water, and drying at room temperature or at 100°. The paper is yellow and keeps well.

### Dry Tests

*Blowpipe test.*—Compounds of zinc when heated upon charcoal with sodium carbonate give an incrustation of the oxide, which is yellow when hot and white when cold. The metal cannot be isolated owing to its volatility and subsequent oxidation. If the incrustation is moistened with a drop of cobalt nitrate solution and again heated, a green mass (Rinmann's green), consisting largely of cobalt zincate  $\text{CoZnO}_2$  is obtained.

An alternative method is to soak a piece of ashless filter paper in the zinc salt solution, add one drop of cobalt nitrate solution and to ignite in a crucible or in a coil of platinum wire. The residue is coloured green.

### DETECTION AND SEPARATION OF THE METALS IN THE ZINC GROUP (GROUP IIIB)

As in previous groups, the student should obtain from the teacher, or prepare for himself, a mixture of some or all of the simple soluble salts of the metals of this group. It is assumed that all the metals of the earlier groups are either absent or have been removed. Add excess of ammonium chloride solution or 1–2 grams of solid ammonium chloride, heat to boiling, add ammonia solution until alkaline and then 1 ml. in excess, and pass hydrogen sulphide, preferably under pressure (Fig. II, 2, 1), for 30–60 seconds. Filter immediately; the addition of a little filter paper pulp (e.g. as a portion of a Whatman filtration accelerator) is beneficial. Test the filtrate for complete precipitation. Wash the precipitate with 1 per cent ammonium chloride solution containing a little saturated hydrogen sulphide water. On occasion, the filtrate is dark-coloured due to the production of colloidal nickel sulphide, which passes through the filter. This is generally prevented by the use of

macerated filter paper, but if it should occur, the filtrate must be acidified with acetic acid and boiled for 30 seconds to coagulate the nickel sulphide: the latter is filtered, washed and combined with the main Group IIIB precipitate.

### III, 28. Table V. Analysis of the Zinc Group (Group IIIB)

The precipitate may contain  $\text{CoS}$ ,  $\text{NiS}$ ,  $\text{MnS}$  and  $\text{ZnS}$ . Wash the ppt. with 1%  $\text{NH}_4\text{Cl}$  solution containing a little saturated  $\text{H}_2\text{S}$  water. (T) Transfer the ppt. to a small beaker and stir with cold dilute  $\text{HCl}$  (1 volume of concentrated acid : 11 volumes of water; *ca. N*) for 2-3 minutes. Filter.

**Residue.** If black, may contain  $\text{CoS}$  and  $\text{NiS}$ . Test residue with borax bead.

Blue bead.

**Co present.**

Dissolve residue in a mixture of 1.5 ml. of 10%  $\text{NaOCl}$  solution and 0.5 ml. of dilute  $\text{HCl}$ . Add 1 ml. of dilute  $\text{HCl}$  and boil until  $\text{Cl}_2$  is expelled. Cool and dilute to about 4 ml. Divide into 2 equal parts.

(i) Add 1 ml. of amyl alcohol, 2 grams of solid  $\text{NH}_4\text{SCN}$ , and shake.

Amyl alcohol layer coloured blue.

**Co present.**

(ii) Add 0.5 ml. of  $\text{NH}_4\text{Cl}$  solution,  $\text{NH}_3$  solution until faintly alkaline, and then a little dimethylglyoxime reagent.

Red ppt.

**Ni present.**

**Filtrate.** May contain  $\text{MnCl}_2$  and  $\text{ZnCl}_2$  (plus, possibly, traces of  $\text{CoCl}_2$  and  $\text{NiCl}_2$ ). Boil until  $\text{H}_2\text{S}$  removed (test with lead acetate paper), cool, add excess of  $\text{NaOH}$  solution, 1 ml. of 3%  $\text{H}_2\text{O}_2$  solution, boil for 3 minutes and filter.

**Residue.** Dark-coloured. May contain  $\text{MnO}_2 \cdot x\text{H}_2\text{O}$  (plus traces of  $\text{Co}(\text{OH})_3$  and  $\text{Ni}(\text{OH})_2$ ). Dissolve the ppt. in 5 ml. of dilute  $\text{HNO}_3$  with the addition of a few drops of 3%  $\text{H}_2\text{O}_2$  solution. Boil to decompose the excess of  $\text{H}_2\text{O}_2$ . Then:

*Either*—Add 1 gram of  $\text{Pb}_3\text{O}_4$  and 3 ml. of concentrated  $\text{HNO}_3$ , boil for 1 minute and allow to settle.

Purple solution of  $\text{HMnO}_4$ .

**Mn present.**

*Or*—To cold solution, add 0.05-0.1 gram of  $\text{NaBiO}_3$ , shake and allow to settle.

Purple solution of  $\text{HMnO}_4$ .

**Mn present.**

**Filtrate.** May contain  $\text{Na}_2[\text{ZnO}_2]$ .

Divide into 2 parts.

(i) Acidify with dilute acetic acid and pass  $\text{H}_2\text{S}$ .

White ppt. of  $\text{ZnS}$ .

**Zn present.**

(ii) Just acidify with dilute  $\text{H}_2\text{SO}_4$ . Use 0.5 ml. of the solution. Add 0.2 ml. of dilute  $\text{Co}(\text{NO}_3)_2$  solution and 0.5 ml. of the ammonium mercuri-thiocyanate reagent and stir.

Pale blue ppt.

**Zn present.**

### III, 28. Table SMV. Analysis of the Zinc Group (Group IIIB)

The ppt. may contain CoS, NiS, MnS and ZnS. If it is not black, CoS and NiS are absent. Wash the ppt. with 1%  $\text{NH}_4\text{Cl}$  solution to which a little saturated  $\text{H}_2\text{S}$  water has been added. (T) Stir the ppt. in the cold with 1 ml. of  $N\text{-HCl}$  (1 volume of concentrated acid : 10-12 parts of water) for 1-2 minutes. Centrifuge.

**Residue.** If black, may contain CoS and NiS. Test residue with borax bead.

Blue bead.

**Co present.**

Add 10-15 drops of dilute  $\text{HCl}$  and 5 drops of 10%  $\text{NaOCl}$  solution, stir and place in a hot water bath for 1-2 minutes. Transfer the liquid with the aid of 1 ml. of water to a semimicro boiling tube and boil gently to expel  $\text{Cl}_2$ . Divide the solution into 2 parts.

(i) Add 0.5-1 ml. of amyl alcohol and 50 mg. of solid  $\text{NH}_4\text{SCN}$ , and shake.

Blue coloration in the alcohol layer.

**Co present.**

(ii) Add 1 drop of  $\text{NH}_4\text{Cl}$  solution, render faintly alkaline with  $\text{NH}_3$  solution, and add 3-5 drops of dimethylglyoxime reagent.

Red ppt.

**Ni present.**

**Centrifugate.** May contain  $\text{MnCl}_2$  and  $\text{ZnCl}_2$  (plus, possibly, traces of  $\text{CoCl}_2$  and  $\text{NiCl}_2$ ).

Transfer to a semimicro boiling tube, boil to expel  $\text{H}_2\text{S}$  (test with lead acetate paper), return liquid to semimicro centrifuge tube, cool, add excess of  $\text{NaOH}$  solution (0.5-1 ml.) and 4 drops of 3%  $\text{H}_2\text{O}_2$  solution; heat on a water bath for 3 minutes. Centrifuge.

**Residue.** Dark-coloured. May contain  $\text{MnO}_2 \cdot x\text{H}_2\text{O}$  (plus traces of  $\text{Co}(\text{OH})_3$  and  $\text{Ni}(\text{OH})_2$ ). Dissolve the ppt. in 0.5 ml. of dilute  $\text{HNO}_3$  and a drop or two of 3%  $\text{H}_2\text{O}_2$  solution. Warm on a water bath for 2-3 minutes to decompose excess of  $\text{H}_2\text{O}_2$ ; cool. Add 50 mg. of  $\text{NaBiO}_3$ , shake and allow to settle.

Purple solution of  $\text{HMnO}_4$ .

**Mn present.**

Alternatively, dissolve the ppt. in 0.5 ml. of dilute  $\text{HNO}_3$  with the addition of 1-2 drops of 3%  $\text{H}_2\text{O}_2$  solution. Transfer to a semimicro boiling tube with the aid of 0.5 ml. of water, and boil to decompose excess of  $\text{H}_2\text{O}_2$ . Cool, add 0.5 ml. of concentrated  $\text{HNO}_3$  and 250 mg. of  $\text{Pb}_3\text{O}_4$ . Boil for 1 minute and allow to stand.

Purple solution of  $\text{HMnO}_4$ .

**Mn present.**

**Centrifugate.** May contain  $\text{Na}_2[\text{ZnO}_2]$ . Divide into 2 parts.

(i) Pass  $\text{H}_2\text{S}$ .

White ppt. of  $\text{ZnS}$ .

**Zn present.**

Use either test (ii) or (iii).

(ii) Just acidify with dilute  $\text{H}_2\text{SO}_4$ , add 5 drops of 0.1%  $\text{CuSO}_4$  solution, and 5 drops of ammonium mercuri-thiocyanate reagent, and stir.

Violet ppt.

**Zn present.**

(iii) Just acidify with dilute  $\text{H}_2\text{SO}_4$ , add a drop of dilute cobalt acetate or nitrate solution, 0.5 ml. of ammonium mercuri-thiocyanate reagent, and stir.

Pale blue ppt.

**Zn present.**

## THE CALCIUM GROUP (GROUP IV)

## BARIUM, STRONTIUM AND CALCIUM

This group comprises the three alkaline earth metals; they are distinguished from the metals of the preceding groups by the fact that their salts are not precipitated by the group reagents for Groups I, II, IIIA and IIIB, and are characterised by their precipitation with ammonium carbonate solution in the presence of moderate concentrations of ammonium chloride and ammonia solutions.

## BARIUM, Ba

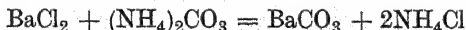
Barium is a silver-white, malleable and ductile metal, which is stable in dry air. It reacts with water at the ordinary temperature forming barium hydroxide and liberating hydrogen. The metal is soluble in acids with the evolution of hydrogen.

III, 29. REACTIONS OF THE BARIUM ION,  $\text{Ba}^{++}$ 

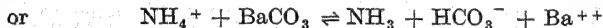
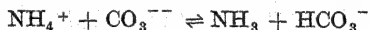
Use a solution of barium chloride,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ .

**1. Ammonia Solution:** no precipitate of barium hydroxide because of its relatively high solubility.\* If the alkaline solution is exposed to the atmosphere, some carbon dioxide is absorbed and a turbidity, due to barium carbonate, is produced.

**2. Ammonium Carbonate Solution†:** white precipitate of barium carbonate, soluble in acetic acid and in dilute mineral acids.

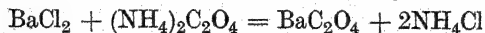


The precipitate is slightly soluble in solutions of ammonium salts of strong acids: this is because the ammonium ion, being a strong acid, reacts with the base, the carbonate ion  $\text{CO}_3^{--}$ , leading to the formation of the bicarbonate ion  $\text{HCO}_3^-$ , and hence the carbonate ion concentration of the solution is decreased:



If the amount of barium carbonate precipitate is very small, it may well dissolve in high concentrations of ammonium salts.

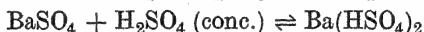
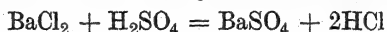
**3. Ammonium Oxalate Solution:** white precipitate of barium oxalate  $\text{BaC}_2\text{O}_4$ , slightly soluble in water (0.09 g. per litre; S.P.  $1.7 \times 10^{-7}$ ), but readily dissolved by hot dilute acetic acid (distinction from calcium) and by mineral acids.



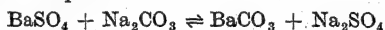
\* A slight turbidity is due to small amounts of ammonium carbonate often present in the reagent.

† Or a solution of any soluble carbonate.

**4. Dilute Sulphuric Acid:** heavy, white, finely-divided precipitate of barium sulphate  $\text{BaSO}_4$ , practically insoluble in water (2.5 milligrams per litre; S.P.  $1.2 \times 10^{-10}$ ), almost insoluble in dilute acids and in ammonium sulphate solution, and appreciably soluble in boiling concentrated sulphuric acid. By precipitation in boiling solution or preferably in the presence of ammonium acetate, a more readily filterable form is obtained.



If barium sulphate is boiled with a concentrated solution of sodium carbonate, partial transformation into the less soluble barium carbonate occurs in accordance with the equation:



Owing to the reversibility of the reaction, the transformation is incomplete. If the mixture is filtered and washed (thus removing the sodium sulphate), and the residue boiled with a fresh volume of sodium carbonate solution, more of the barium sulphate will be converted into barium carbonate. By repetition of this process, practically all of the sulphate can be converted into the corresponding carbonate. The carbonate may be dissolved in acids; this process therefore provides a method for bringing insoluble sulphates into solution. A more expeditious method of obtaining the same result is to fuse the barium sulphate with 4-6 times its weight of anhydrous sodium carbonate; the maximum concentration of carbonate is thus obtained and the reaction proceeds almost to completion in one operation (compare Law of Mass Action, Section I, 9). The melt is allowed to cool, extracted with boiling water and filtered; the residue of barium carbonate can then be dissolved in the appropriate acid. It has been stated that by boiling barium sulphate with at least 15 times its equivalent weight of 1-2*M* sodium carbonate solution, 99 per cent is converted into barium carbonate in 1 hour.

**5. Saturated Calcium Sulphate Solution:** immediate white precipitate of barium sulphate. A similar but more trustworthy result is obtained with saturated strontium sulphate solution.



**6. Potassium Chromate Solution:** yellow precipitate of barium chromate  $\text{BaCrO}_4$ , practically insoluble in water (3.8 milligrams per litre; S.P.  $2.3 \times 10^{-10}$ ) and in dilute acetic acid (distinction from strontium and calcium), but readily soluble in mineral acids (compare Sections I, 17 and IV, 23).



The addition of acid to potassium chromate solution causes the yellow colour of the solution to change to reddish-orange, due to the formation of dichromate:

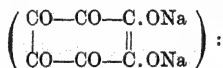


Upon adding a base (e.g.  $\text{OH}^-$  ions) to a dichromate, the  $\text{H}^+$  ions will be removed, the reaction will proceed from right to left, i.e.

chromate will form. In the presence of a large concentration of hydrogen ions, the chromate ion concentration will be reduced to such a value that the solubility product of  $\text{BaCrO}_4$  will not be attained. Hence to precipitate  $\text{Ba}^{++}$  ions as  $\text{BaCrO}_4$ , strong acids must be removed or neutralised. The addition of sodium acetate acts as a buffer by reducing the hydrogen ion concentration and complete precipitation of  $\text{BaCrO}_4$  will take place.

The solubility products for  $\text{SrCrO}_4$  and  $\text{CaCrO}_4$  are much larger than for  $\text{BaCrO}_4$  and hence they require a larger  $\text{CrO}_4^{--}$  ion concentration to precipitate them. The addition of acetic acid to the  $\text{K}_2\text{CrO}_4$  solution lowers the  $\text{CrO}_4^{--}$  ion concentration sufficiently to prevent the precipitation of  $\text{SrCrO}_4$  and  $\text{CaCrO}_4$  but is maintained high enough to precipitate  $\text{BaCrO}_4$ .

#### †7. Sodium Rhodizonate Reagent



reddish-brown precipitate of the barium salt of rhodizonic acid in neutral solution. Calcium and magnesium salts do not interfere: strontium salts react like those of barium, but only the precipitate due to the former is completely soluble in dilute hydrochloric acid. Other elements, *e.g.* those precipitated by hydrogen sulphide and by ammonium sulphide, should be absent. The reagent should be confined to testing for elements in Group IV (calcium group).

Place a drop of the neutral or faintly acid test solution upon drop-reaction paper and add a drop of the reagent. A brown or reddish-brown spot is obtained.

Sensitivity: 0.25  $\mu\text{g}$ . Ba. Concentration limit: 1 in 200,000.

The reagent consists of a 0.5 per cent aqueous solution of sodium rhodizonate. It does not keep well so that only small quantities should be prepared at a time.

In the presence of strontium the reddish-brown stain of barium rhodizonate is treated with 0.5N-hydrochloric acid; the strontium rhodizonate dissolves, whilst the barium derivative is converted into the brilliant red acid salt. The reaction is best carried out on drop-reaction paper as above.

Treat the reddish-brown spot with a drop of 0.5N hydrochloric acid when a bright red stain is formed if barium is present. If barium is absent, the spot disappears.

Sensitivity: 0.5  $\mu\text{g}$ . Ba in the presence of 50 times the amount of Sr.

Concentration limit: 1 in 90,000.

#### Dry Test

*Flame coloration.*—Barium salts, when heated in the non-luminous Bunsen flame, impart a yellowish-green colour to the flame. Since most barium salts, with the exception of the chloride, are non-volatile, the platinum wire is moistened with concentrated hydrochloric acid before being dipped into the

substance. The sulphate is first reduced to the sulphide in the reducing flame, then moistened with concentrated hydrochloric acid, and re-introduced into the flame.

#### STRONTIUM, Sr

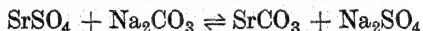
Strontium is a silver-white, malleable and ductile metal. Its properties are similar to those of barium.

### III, 30. REACTIONS OF THE STRONTIUM ION, $\text{Sr}^{++}$

Use a solution of strontium chloride,  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ .

1. **Ammonia Solution:** no precipitate.
2. **Ammonium Carbonate Solution:** white precipitate of strontium carbonate  $\text{SrCO}_3$ , less soluble in water than barium carbonate. Its slight solubility in ammonium salts of strong acids is similar to that of  $\text{BaCO}_3$  (see Section III, 29, reaction 2).

3. **Dilute Sulphuric Acid:** white precipitate of strontium sulphate  $\text{SrSO}_4$ , very sparingly soluble in water (0.110 g. per litre; S.P.  $3.6 \times 10^{-7}$ ), insoluble in ammonium sulphate solution even on boiling (distinction from calcium) and slightly soluble in boiling hydrochloric acid. It is almost completely converted into the corresponding carbonate by boiling with a concentrated solution of sodium carbonate.



4. **Saturated Calcium Sulphate Solution:** white precipitate of strontium sulphate, formed slowly in the cold but more rapidly on boiling (distinction from barium).

5. **Ammonium Oxalate Solution:** white precipitate of strontium oxalate, sparingly soluble in water (0.66 g. per litre; S.P.  $1.4 \times 10^{-7}$ ) and in acetic acid, but soluble in mineral acids.

6. **Potassium Chromate Solution:** yellow precipitate of strontium chromate  $\text{SrCrO}_4$  from concentrated solutions; the precipitate is appreciably soluble in water (1.2 grams per litre) and in acetic acid. No precipitation therefore occurs in dilute solutions nor from concentrated solutions containing acetic acid (distinction from barium; see Section III, 29, reaction 6).

- †7. **Sodium Rhodizonate Reagent:** reddish-brown precipitate of strontium rhodizonate in neutral solution. The test is applied to the elements of Group IV (calcium group). Barium reacts similarly and a method for the detection of barium in the presence of strontium has already been described (Section III, 29, reaction 7). To detect strontium in the presence of barium, the latter is converted into the insoluble



barium chromate. Barium chromate does not react with sodium rhodizonate, but the more soluble strontium chromate reacts normally.

If **barium is absent**, place a drop of the neutral test solution on drop-reaction paper or on a spot plate, and add a drop of the reagent. A brownish-red coloration or precipitate is produced.

Sensitivity: 4  $\mu$ g. Sr. Concentration limit: 1 in 13,000.

If **barium is present**, proceed as follows. Impregnate some quantitative filter paper or drop-reaction paper with a saturated solution of potassium chromate, and dry it. Place a drop of the test solution on this paper and, after a minute, place 1 drop of the reagent on the moistened spot. A brownish-red spot or ring is formed.

Sensitivity: 4  $\mu$ g. Sr in the presence of 80 times the amount of Ba.

Concentration limit: 1 in 13,000.

For further details of the reagent, see under Barium, Section III, 29, reaction 7.

## Dry Test

*Flame coloration.*—Volatile strontium compounds, especially the chloride, impart a characteristic carmine-red colour to the non-luminous Bunsen flame (see remarks under Barium).

### CALCIUM, Ca

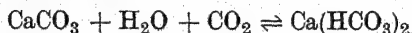
Calcium, like the other elements of this group, is a silver-white metal and possesses similar properties. It is, however, only slightly attacked by concentrated nitric acid.

## III, 31. REACTIONS OF THE CALCIUM ION, $\text{Ca}^{++}$

Use a solution of calcium chloride,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ .

1. **Ammonia Solution:** no precipitate. The result is similar to that for barium ions.

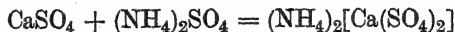
2. **Ammonium Carbonate Solution:** white amorphous precipitate of calcium carbonate  $\text{CaCO}_3$ , which becomes crystalline on boiling. The precipitate is soluble in water containing excess of carbonic acid, due to the formation of the soluble bicarbonate. This remark applies also to the carbonates of strontium and barium.



Calcium carbonate is slightly soluble in solutions of ammonium salts of strong acids (compare  $\text{BaCO}_3$ , Section III, 29, reaction 2).

3. **Dilute Sulphuric Acid:** white precipitate of calcium sulphate  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  from concentrated solutions (see reaction 10 below). The precipitate is appreciably soluble in

water (2.0 grams per litre at 25°; S.P.  $2.3 \times 10^{-4}$ ), is more soluble in acids than either strontium or barium sulphates, and is readily soluble in hot concentrated ammonium sulphate solution owing to the formation of a complex salt (distinction from strontium).

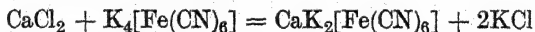


**4. Saturated Calcium Sulphate Solution:** no precipitate (difference from strontium and barium).

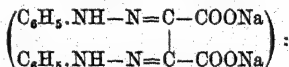
**5. Ammonium Oxalate Solution:** white precipitate of calcium oxalate  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ , immediately from concentrated solutions and slowly from dilute solutions. Precipitation is facilitated by making the solution alkaline with ammonia solution. The precipitate is practically insoluble in water (8 milligrams per litre at 20°; S.P.  $3.8 \times 10^{-9}$ ), insoluble in acetic acid, but readily dissolved by mineral acids (compare Section I, 17).

**6. Potassium Chromate Solution:** no precipitate in dilute solutions (solubility 23 grams per litre) nor from concentrated solutions containing free acetic acid (compare Section III, 29, reaction 6).

**7. Potassium Ferrocyanide Solution:** white precipitate of calcium potassium ferrocyanide  $\text{CaK}_2[\text{Fe}(\text{CN})_6]$  is produced by excess of the reagent. The test is more sensitive in the presence of excess of ammonium chloride solution; a white precipitate of calcium potassium ammonium ferrocyanide of variable composition is formed (distinction from strontium). Large amounts of barium and of magnesium interfere, since they give a similar reaction.



†8. Sodium Dihydroxytartrate Osazone Reagent



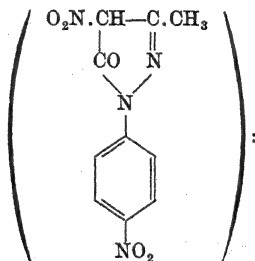
yellow sparingly-soluble precipitate of the calcium salt. All other metals, with the exception of alkali and ammonium salts, must be absent. Magnesium does not interfere provided its concentration does not exceed 10 times that of the calcium.

Place a drop of the neutral test solution on a black spot plate or upon a black watch glass, and add a tiny fragment of the solid reagent. If calcium is absent, the reagent dissolves completely. The presence of calcium is revealed by the formation over the surface of the liquid of a white film which ultimately separates as a dense precipitate.

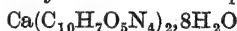
Sensitivity: 0.01  $\mu\text{g}$ . Ca. Concentration limit: 1 in 5,000,000.

The reagent is useful *inter alia* for the rapid differentiation between tap and distilled water: a positive result is obtained with a mixture of 1 part of tap water and 30 parts of distilled water.

†9. Picrolonic Acid (or 1-*p*-Nitrophenyl-3-methyl-4-nitro-5-pyrazolone) Reagent



characteristic rectangular crystals of calcium picrolonate



in neutral or acetic acid solutions. Strontium and barium give precipitates but of different crystalline form. Numerous elements, including copper, lead, thorium, iron, aluminium, cobalt, nickel and barium, interfere.

Place a drop of the test solution (either neutral or acidified with acetic acid) in the depression of a warm spot plate and add 1 drop of a saturated aqueous solution of picrolonic acid. Characteristic rectangular crystals are produced.

Sensitivity: 100  $\mu\text{g}$ . (in 5 ml.). Concentration limit: 1 in 50,000.

The sensitivity is 0.01  $\mu\text{g}$ . (in 0.01 ml.) under the microscope.

†10. Calcium Sulphate Dihydrate (Microscope) Test.—This is an excellent confirmatory test for calcium in Group IV; it involves the use of a microscope (magnification about 110 $\times$ ). The salts should preferably be present as nitrates.

Evaporate a few drops of the test solution on a watch glass to dryness on a water bath, dissolve the residue in a few drops of water, transfer to a microscope slide, and add a minute drop of dilute sulphuric acid. (It may be necessary to warm the slide gently on a water bath until crystallisation just sets in at the edges.) Upon observation through a microscope, bundles of needles or elongated prisms will be visible if calcium is present.

Concentration limit: 1 in 6,000.

It may be noted that barium and strontium nitrates are practically insoluble in absolute ethyl alcohol and also in 83 per cent nitric acid, whilst calcium nitrate is very soluble in absolute alcohol and fairly soluble in the concentrated nitric acid. The best method for separating Sr and Ca makes use of 83 per cent nitric acid (see the various Group IV separation tables).

## Dry Test

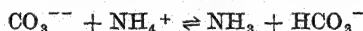
*Flame coloration.*—Volatile calcium compounds impart a yellowish-red colour to the Bunsen flame (see remarks under Barium).

DETECTION AND SEPARATION OF THE METALS IN THE CALCIUM GROUP  
(GROUP IV)

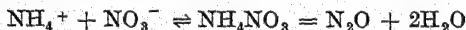
It is assumed that the metals of Groups I to IIIB have been removed as already described, or that only metals of the alkaline earth group are present. As in previous group separations, the student should prepare or obtain from the teacher a solution containing some or all of the simple salts of the metals of Group IV.

The filtrate from Group IIIB, if employed, should be evaporated to dryness (moist paste) in an evaporating dish [FUME CUPBOARD], allowed to cool, and about 4 ml. of concentrated nitric acid added slowly and in such a manner as to wash down the precipitate on the sides to the bottom of the dish. Evaporation is then continued cautiously until dry and then more strongly until no more fumes of ammonium chloride are evolved. The residue is allowed to cool, dissolved in a little dilute hydrochloric acid, transferred to a test-tube, and a little ammonium chloride solution added. The clear solution may then be treated with ammonia solution until alkaline and Group IV precipitated with ammonium carbonate solution.

The reason for the above operation is that the filtrate from Group IIIB contains a very high concentration of ammonium salts—far higher than is necessary to prevent the precipitation of magnesium hydroxide. The excessive concentration of ammonium ions will lower the  $\text{CO}_3^{--}$  ion concentration of the solution (when ammonium carbonate solution is added) to such an extent that appreciable amounts of the carbonates of Ba, Sr and Ca may not be precipitated:

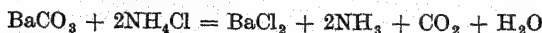


The effect is due to the acidic properties of the ammonium ion, which acts as a donor of protons to the carbonate ion. For this reason, it is recommended that practically all the ammonium salts be eliminated with concentrated nitric acid:



The latter reaction takes place at a lower temperature than that necessary to remove ammonium salts by sublimation.

It may be noted that the precipitation with ammonium carbonate takes place in hot solution, due to the fact that the carbonates are thus obtained in a more granular form and are therefore more easily filtered and washed. The solution must not be boiled as this decomposes the reagent and may result in some redissolution of the carbonates:



When reprecipitating  $\text{SrCO}_3$  and/or  $\text{CaCO}_3$  in the subsequent separation, it is probably better to use a little  $\text{Na}_2\text{CO}_3$  than  $(\text{NH}_4)_2\text{CO}_3$ .

### III, 32. Table VI. Analysis of the Calcium Group (Group IV)

Add 1–2 ml. of  $\text{NH}_4\text{Cl}$  solution,  $\text{NH}_3$  solution until just basic, followed by  $(\text{NH}_4)_2\text{CO}_3$  solution until precipitation is complete. Heat on a water bath, with stirring, at  $60\text{--}70^\circ\text{C}$  for 5 minutes. Filter, wash with a little hot water and discard the filtrate and washings.

The residue may contain  $\text{BaCO}_3$ ,  $\text{SrCO}_3$  and  $\text{CaCO}_3$ . (T) Dissolve the ppt. in 5 ml. of hot 2*N* acetic acid by pouring the acid repeatedly through the filter paper. Test 1 ml. for barium by adding  $\text{K}_2\text{CrO}_4$  solution dropwise to the nearly boiling solution. A yellow ppt. indicates Ba.

**Ba present.**—Heat the remainder of the solution almost to boiling, and add a slight excess of  $\text{K}_2\text{CrO}_4$  solution (*i.e.* until the solution assumes a yellow tint). Filter and wash the ppt. (C) with a little hot water. Render the hot filtrate and washings basic with  $\text{NH}_3$  solution and add an excess of  $(\text{NH}_4)_2\text{CO}_3$  solution or, better, a little solid  $\text{Na}_2\text{CO}_3$ . A white ppt. indicates the presence of  $\text{SrCO}_3$  and/or  $\text{CaCO}_3$ . Wash the ppt. with hot water, and dissolve it in 4 ml. of warm 2*N*-acetic acid: boil to remove excess of  $\text{CO}_2$  (solution A).

**Ba absent.**—Discard the portion used in testing for barium, and employ the remainder of the solution (B), after boiling for 1 minute to expel  $\text{CO}_2$ , to test for strontium and calcium.

#### Residue (C).

Yellow:  $\text{BaCrO}_4$ .

Wash well with hot water. Dissolve the ppt. in a little concentrated  $\text{HCl}$ , evaporate almost to dryness, and apply the flame test.

Green (or yellowish-green) flame.

**Ba present.**

(Use spectroscope, if available.)

**Solution A or Solution B.** The volume should be about 4 ml.

*Either*—To 2 ml. of the cold solution, add 2 ml. of saturated  $(\text{NH}_4)_2\text{SO}_4$  solution, followed by 0.2 gram of sodium thiosulphate, heat in a beaker of boiling water for 5 minutes, and allow to stand for a short time. Filter.

*Or*—To 2 ml. of the solution, add 2 ml. of triethanolamine, 2 ml. of saturated  $(\text{NH}_4)_2\text{SO}_4$  solution, heat on a boiling water bath with vigorous stirring for 5 minutes, and allow to stand for 1–2 minutes. Dilute with an equal volume of water and filter.

**Residue.** Largely  $\text{SrSO}_4$ . Wash with a little water. Transfer ppt. and filter paper to a small crucible, heat until paper has charred (or burn filter paper and ppt., held in a Pt wire, over a crucible), moisten ash with a few drops of concentrated  $\text{HCl}$  and apply the flame test.

Crimson flame.

**Sr present.**

(Use spectroscope, if available.)

**Filtrate.** May contain Ca complex. (If Sr absent, use 2 ml. of solution A or B.) Add a little  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution\* and warm on a water bath.

White ppt. of  $\text{CaC}_2\text{O}_4$ .

**Ca present.**

Confirm by flame test on ppt.—brick-red flame.

(Use spectroscope, if available.)

\* When triethanolamine has been employed in the separation of Sr and Ca, the addition of a little acetic acid (*i.e.* until the solution is faintly acid) may assist the precipitation of the  $\text{CaC}_2\text{O}_4$ .

### III, 32. Table SMVI. Analysis of the Calcium Group (Group IV)

Add a few drops of  $\text{NH}_4\text{Cl}$  solution, render alkaline with concentrated  $\text{NH}_3$  solution and add, with stirring, 0.5 ml. of  $(\text{NH}_4)_2\text{CO}_3$  solution (1). Heat on a water bath to  $60\text{--}70^\circ\text{C}$ , with stirring, for several minutes. Centrifuge.

**Residue.** May contain  $\text{BaCO}_3$ ,  $\text{SrCO}_3$  and  $\text{CaCO}_3$ . Wash with a little hot water and reject washings. (T) Treat the ppt. with 0.5 ml. of dilute acetic acid and stir. Place in a hot water bath until the ppt. has dissolved. Dilute with 0.5 ml. of water. Test 3–4 drops of the hot solution for barium by adding a drop or two of  $\text{K}_2\text{CrO}_4$  solution. A yellow ppt. ( $\text{BaCrO}_4$ ) indicates **Ba present**.

**Centrifugate**  
Discard.

**Ba present.**—To the remainder of the hot solution add a slight excess of  $\text{K}_2\text{CrO}_4$  solution (i.e. until the solution acquires an orange tint), and separate the ppt. of  $\text{BaCrO}_4$  (C) by centrifugation. Render the centrifugate alkaline with  $\text{NH}_3$  solution, and add excess of  $(\text{NH}_4)_2\text{CO}_3$  solution or, better, a little solid  $\text{Na}_2\text{CO}_3$ . Place the tube in the hot water bath. A white ppt. indicates  $\text{SrCO}_3$  and/or  $\text{CaCO}_3$ . Centrifuge and wash with a little hot water. Dissolve the ppt. in 0.5–1 ml. of dilute acetic acid, and place the tube in a hot water bath to remove the excess of  $\text{CO}_2$  (solution A).

**Ba absent.**—Discard the portion used in testing for barium, and employ the remainder of the solution (B) in testing for strontium and calcium after heating on a water bath for a few minutes to expel  $\text{CO}_2$ .

**Residue (C).**  
Yellow:  $\text{BaCrO}_4$ .

Wash with hot water. Dissolve in a few drops of concentrated  $\text{HCl}$ , evaporate almost to dryness in a small crucible, and apply the flame test.

Green (or yellowish-green) flame.

**Ba present.**  
(Use spectroscope, if available.)

**Solution A or Solution B.** Adjust volume to 2 ml. (solution D) by evaporation or dilution as necessary.

*Either*—To 1 ml. of solution, add 1 ml. of saturated  $(\text{NH}_4)_2\text{SO}_4$  solution followed by 0.1 gram of sodium thiosulphate, heat on a water bath for 5 minutes, and allow to stand for a short time. Centrifuge.

*Or*—To 1 ml. of solution, add 1 ml. of triethanolamine and 1 ml. of saturated  $(\text{NH}_4)_2\text{SO}_4$  solution, heat on a water bath with stirring for 5 minutes, and allow to stand for 1–2 minutes. Centrifuge.

**Residue.** Largely  $\text{SrSO}_4$ . Wash with a little water. Stir the ppt. with 3–4 drops of water, transfer the suspension by means of a capillary dropper to 1 sq. cm. of quantitative filter paper contained in a 5 ml. crucible. Ignite until paper has charred, add 1–2 drops of concentrated  $\text{HCl}$ , and apply the flame test.

Crimson flame.

**Sr present.**  
(Use spectroscope, if available.)

**Centrifugate.**  
May contain Ca complex. (If Sr absent, use 1 ml. of solution D.) Add a few drops of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution (2) and warm on a water bath.

White ppt. of  $\text{CaC}_2\text{O}_4$ .

**Ca present.**  
Confirm by flame test—brick-red flame.

(Use spectroscope, if available.)

### III, 32. Table SMVIA. Analysis of Calcium Group (Group IV)

Add a few drops of  $\text{NH}_4\text{Cl}$  solution, make alkaline with concentrated  $\text{NH}_3$  solution and add, with stirring, 0.5 ml. of  $(\text{NH}_4)_2\text{CO}_3$  solution (1). Heat on a water bath to 60–70°C, with stirring, for several minutes. Centrifuge.

**Residue.** May contain  $\text{BaCO}_3$ ,  $\text{SrCO}_3$  and  $\text{CaCO}_3$ . Wash well with a little hot water and reject washings. (T) Treat the ppt. with 0.5 ml. of dilute acetic acid, place in a hot water bath and stir until dissolved. Dilute with 0.5 ml. of water. Test 3–4 drops of the hot solution for barium by adding a drop or two of  $\text{K}_2\text{CrO}_4$  solution. A yellow ppt. ( $\text{BaCrO}_4$ ) indicates **Ba present**.

**Centrifugate.**  
Discard.

**Ba present.**—To the remainder of the hot solution add a slight excess of  $\text{K}_2\text{CrO}_4$  solution (*i.e.* until the solution just assumes an orange tint), and centrifuge the ppt. of  $\text{BaCrO}_4$  (C). Transfer the centrifugate (solution A) by means of a capillary dropper to another centrifuge tube: wash the ppt. with 0.5 ml. of water and combine the washings with solution A.

**Ba absent.**—Discard the portion used in testing for barium, and employ the remainder of the solution (B) in testing for strontium and calcium after heating on a water bath for a few minutes to expel  $\text{CO}_2$ .

**Residue (C).**  
Yellow:  $\text{BaCrO}_4$ .

Dissolve in a few drops of concentrated  $\text{HCl}$ , evaporate to dryness in a small crucible and apply the flame test. Green (or yellowish-green) flame.

**Ba present.**  
(Use spectro-scope, if available.)

**Solution A or Solution B.** Render alkaline with  $\text{NH}_3$  solution, and add excess of  $(\text{NH}_4)_2\text{CO}_3$  solution or, better, a little solid  $\text{Na}_2\text{CO}_3$ . Place the tube in a hot water bath. A white ppt. indicates the presence of  $\text{SrCO}_3$  and/or  $\text{CaCO}_3$ . Centrifuge: discard centrifugate. Wash with 0.5 ml. of hot water and centrifuge: remove the supernatant liquid *as completely as possible* with a capillary dropper. Add 4 drops of 83%  $\text{HNO}_3$  (2), and cool in a stream of cold water from the tap. Add further 4–5 drop portions of 83%  $\text{HNO}_3$ , with stirring, from a T.K. dropping bottle until 2 ml. (3) are introduced. Stir for 3–4 minutes, and centrifuge.

**Residue.**

White:  
 $\text{Sr}(\text{NO}_3)_2$ .  
**Sr present.**  
Confirm by flame test.  
Crimson flame.

(Use spectro-scope, if available.)

**Centrifugate (D).** May contain  $\text{Ca}(\text{NO}_3)_2$ . Transfer *most* of the liquid to a semimicro boiling tube or a small crucible, and evaporate almost to dryness (FUME CUPBOARD). Transfer to a centrifuge tube with the aid of 0.5–1 ml. of water, render alkaline with  $\text{NH}_3$  solution, and add excess of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution (4). Allow to stand in a hot water bath for 2–3 minutes.

White ppt. of  $\text{CaC}_2\text{O}_4$ .

**Ca present.**

Centrifuge, and confirm Ca in the ppt. by the flame test—brick-red flame.

(Use spectro-scope, if available.)

Alternatively, confirm Ca by the  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (microscope) test (5).

## NOTES TO TABLE SMVI

*Notes.* (1) If the filtrate from Group IIIB is employed, it is necessary to remove the excess of ammonium salts. Evaporate to a moist paste in a small crucible, allow to cool, add 1 ml. of concentrated  $\text{HNO}_3$  (by means of a dropper) around the walls of the crucible so as to wash most of the adhering salt to the centre. Heat (FUME CUPBOARD) cautiously at first and then more strongly until no further fumes of ammonium salts are evolved. Allow to cool, add 5 drops of dilute  $\text{HCl}$  and 15 drops of water, transfer the solution to a centrifuge tube, rinse the crucible with 10 drops of water and combine the rinsings with the solution in the tube. To the clear solution add a few drops of  $\text{NH}_4\text{Cl}$  solution, render alkaline with concentrated ammonia solution, and add 0.5 ml. of  $(\text{NH}_4)_2\text{CO}_3$  solution with stirring. Heat on a water bath, with stirring, at  $60\text{--}70^\circ\text{C}$  for a few minutes. Centrifuge.

(2) If triethanolamine has been employed in the separation of Sr and Ca, the addition of a little acetic acid until faintly acid may assist the precipitation.

## NOTES TO TABLE SMVIA

*Notes.* (1) See Note 1 to Table SMVI.

(2) The 83 per cent  $\text{HNO}_3$  (in which  $\text{Sr}(\text{NO}_3)_2$  is almost insoluble) is prepared by adding 100 grams (68.0 ml.) of concentrated  $\text{HNO}_3$  (sp. gr. 1.42: ca. 70%) to 100 grams (66.2 ml.) of fuming  $\text{HNO}_3$  (sp. gr. 1.5: ca. 95%).

(3) The T.K. bottle, charged with 83 per cent  $\text{HNO}_3$ , should be calibrated. The acid should be added dropwise to a clean 5 ml. measuring cylinder until the 2 ml. mark is reached and the number of drops counted. It is advisable to place a small label on the T.K. bottle stating the number of drops per ml.

(4) The addition of dilute acetic acid until faintly acid may assist the precipitation of the  $\text{CaC}_2\text{O}_4$ .

(5) Place 1 drop of the centrifugate *D* on a microscope slide and add 1 drop of dilute  $\text{H}_2\text{SO}_4$ . Concentrate by placing the slide on a micro crucible and warming gently until crystallisation just commences. Examine the crystals in a microscope (magnification: ca.  $\times 100$ ). Bundles of needles or elongated prisms confirm Ca.

## THE ALKALI GROUP (GROUP V)

*MAGNESIUM, SODIUM, POTASSIUM AND AMMONIUM*

The metals of this group are not precipitated by the earlier group reagents. Sodium and potassium belong to the alkali metal group; ammonium is included in this group since its compounds resemble those of the alkali metals, particularly those of potassium. Magnesium, although associated with the alkaline earths in the periodic table, is incorporated in this group because its carbonate is not precipitated by ammonium carbonate solution in the presence of ammonium chloride.

## MAGNESIUM, Mg

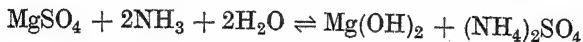
Magnesium is a white, malleable and ductile metal which burns in air or oxygen with a brilliant white light, forming the oxide  $\text{MgO}$  and a little nitride  $\text{Mg}_3\text{N}_2$ . The metal is slowly decomposed by water at the ordinary temperature but rapidly at  $100^\circ$ . It is readily soluble in acids liberating hydrogen. The salts may be regarded as derived from the basic oxide  $\text{MgO}$ .



### III, 33. REACTIONS OF THE MAGNESIUM ION, $\text{Mg}^{++}$

Use a solution of magnesium sulphate,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ .

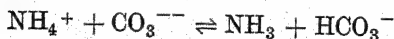
**1. Ammonia Solution:** partial precipitation of white, gelatinous magnesium hydroxide  $\text{Mg}(\text{OH})_2$ , very sparingly soluble in water (12 milligrams per litre; S.P.  $3.4 \times 10^{-11}$ ), but readily soluble in solutions of ammonium salts.



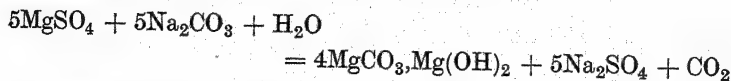
As the reaction progresses, the concentration of the ammonium ions, due to the dissociation of the completely ionised ammonium salt, increases and consequently the concentration of the hydroxyl ions decreases owing to the common ion effect (compare Section I, 14). The small hydroxyl ion concentration, already low, is decreased still further so that much of the magnesium salt remains in solution. In the presence of a sufficient concentration of ammonium salts, the hydroxyl ion concentration is reduced to such an extent that the solubility product of  $\text{Mg}(\text{OH})_2$  is not exceeded (compare Section I, 15); hence magnesium is not precipitated by ammonia solution in the presence of ammonium chloride or other ammonium salts.

**2. Sodium Hydroxide Solution:** white precipitate of magnesium hydroxide, insoluble in excess of the reagent, but readily soluble in solutions of ammonium salts.

**3. Ammonium Carbonate Solution:** white precipitate of basic magnesium carbonate, often only on boiling or on long standing. No precipitate is obtained in the presence of ammonium salts of strong acids, since the high concentration of ammonium ions will lower the  $\text{CO}_3^{--}$  ion concentration of the solution when ammonium carbonate is added to so low a value that the solubility product of  $\text{MgCO}_3$  ( $2.6 \times 10^{-5}$ ) is not attained:

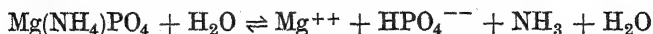


**4. Sodium Carbonate Solution:** white voluminous precipitate of basic carbonate  $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$  or  $[\text{Mg}(\text{MgCO}_3)_4](\text{OH})_2$ , insoluble in solutions of bases, but soluble in acids and in solutions of ammonium salts.



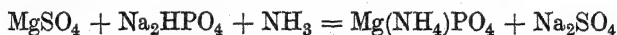
**5. Sodium Phosphate Solution:** white crystalline precipitate of magnesium ammonium phosphate  $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$  in the presence of ammonium chloride (to prevent the precipitation of magnesium hydroxide) and ammonia solutions; the precipitate is sparingly soluble in water, soluble in acetic acid and

in mineral acids. The normal solubility of  $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$  is increased by its hydrolysis in water:



this tendency is reduced by moderate amounts of ammonia (it is found that the compound is very sparingly soluble in 2.5 per cent ammonia solution). The precipitate separates slowly from dilute solutions because of its tendency to form super-saturated solutions; this may usually be overcome by cooling and by rubbing the test-tube or beaker beneath the surface of the liquid with a glass rod.

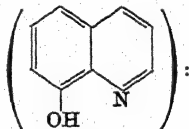
A white flocculent precipitate of magnesium hydrogen phosphate  $\text{MgHPO}_4$  is produced in *neutral* solutions.



**6. Diphenyl-carbazide Reagent** ( $\text{C}_6\text{H}_5 \cdot \text{NH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$ ).—The magnesium salt solution is treated with sodium hydroxide solution—a precipitate of magnesium hydroxide will be formed—then with a few drops of the diphenyl-carbazide reagent and the solution filtered. On washing the precipitate with hot water, it will be seen to have acquired a violet-red colour, due to the formation of a complex salt or an adsorption complex. Metals of Groups II and III interfere and should therefore be absent.

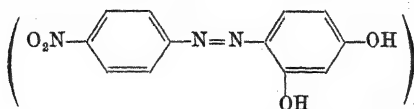
The reagent is prepared by dissolving 0.2 gram of diphenyl-carbazide in 10 ml. of glacial acetic acid and diluting to 100 ml. with rectified spirit.

### 7. 8-Hydroxy-quinoline or "Oxine" Reagent



When a solution of a magnesium salt, containing a little ammonium chloride, is treated with 1–2 ml. of the reagent which has been rendered strongly ammoniacal by the addition of 3–4 ml. of dilute ammonia solution and the mixture heated to the boiling point, a yellow precipitate of the complex salt  $\text{Mg}(\text{C}_9\text{H}_6\text{N}_2\text{O})_2 \cdot 4\text{H}_2\text{O}$  is obtained. All other metals, except sodium and potassium, must be absent.

The reagent is prepared by dissolving 2 grams of oxine in 100 ml. of 2*N* acetic acid.

8. *para*-Nitrobenzene-azo-resorcinol (or Magneson I)

**Reagent.**—This test depends upon the adsorption of the reagent, which is a dyestuff, upon  $\text{Mg}(\text{OH})_2$  in alkaline solution whereby a blue lake (compare Section I, 43) is produced. Two ml. of the test solution, slightly acid with hydrochloric acid, is treated with 1 drop of the reagent and sufficient *N* sodium hydroxide solution to render the solution strongly alkaline, say 2–3 ml. A blue precipitate appears. This is an excellent confirmatory test in macro analysis, but it is essential to perform a blank test with the reagents, which frequently yield a blue coloration. For this reason a blue precipitate should be looked for. All metals, except those of the alkalis, must be absent. Ammonium salts reduce the sensitivity of the test by preventing the precipitation of  $\text{Mg}(\text{OH})_2$ , and should therefore be eliminated.

The reagent (for macro analysis) consists of a 0.5 per cent solution of *p*-nitrobenzene-azo-resorcinol in 0.25*N* sodium hydroxide.

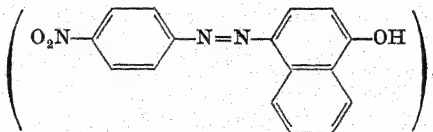
† The spot-test technique is as follows. Place a drop of the test solution on a spot plate and add 1–2 drops of the reagent. It is essential that the solution be strongly alkaline; the addition of 1 drop of *N* sodium hydroxide may be advisable. According to the concentration of magnesium a blue precipitate is formed or the reddish-violet reagent assumes a blue colour. A comparative test on distilled water should be carried out.

Sensitivity: 0.5  $\mu\text{g}$ . Mg. Concentration limit: 1 in 100,000.

Filter or drop-reaction paper should not be used.

The reagent is prepared by dissolving 0.001 gram of the dyestuff in 100 ml. of *N* sodium hydroxide.

An alternative agent is *para*-nitrobenzene-azo- $\alpha$ -naphthol or Magneson II



It yields the same colour changes as Magneson I, but has the advantage that it is more sensitive (sensitivity: 0.2  $\mu\text{g}$ . Mg; concentration limit: 1 in 250,000) and its tinctorial power is less so that the blank test is not so deeply coloured. Its mode of use and preparation are identical with that described above for Magneson I.

†9. **Titan Yellow Reagent.**—Titan yellow (also known as Clayton Yellow and Thiazole Yellow) is a water-soluble yellow dyestuff. It is adsorbed by magnesium hydroxide producing a deep red colour or precipitate. Barium and calcium do not react but intensify the red colour. All elements of Groups I to IIIB should be removed before applying the test.

Place a drop of the test solution on a spot plate, introduce a drop of reagent and a drop of 0.1N sodium hydroxide. A red colour or precipitate is produced.

An alternative technique is to treat 0.5 ml. of the neutral or slightly acidic test solution with 0.2 ml. of the reagent and 0.5 ml. of 0.1N sodium hydroxide solution. A red precipitate or coloration is produced.

Sensitivity: 1.5  $\mu$ g. Mg. Concentration limit: 1 in 33,000.

The reagent consists of a 0.1 per cent aqueous solution of titan yellow.

†10. **Quinalizarin\* Reagent:** blue precipitate or cornflower-blue coloration with magnesium salts. The coloration can be readily distinguished from the blue-violet colour of the reagent. Upon the addition of a little bromine water, the colour disappears (difference from beryllium). The alkaline earth metals and aluminium do not interfere under the conditions of the test, but all elements of Groups I to IIIB should be removed. Phosphates and large amounts of ammonium salts decrease the sensitivity of the reaction.

Place a drop of the test solution and a drop of distilled water in adjacent cavities of a spot plate and add 2 drops of the reagent to each. If the solution is acid, it will be coloured yellowish-red by the reagent. Add 2N sodium hydroxide until the colour changes to violet and a further excess to increase the volume by 25 to 50 per cent. A blue precipitate or coloration appears. The blank test has a blue-violet colour.

Sensitivity: 0.25  $\mu$ g. Mg. Concentration limit: 1 in 200,000.

The reagent is prepared by dissolving 0.01–0.02 gram of quinalizarin in 100 ml. of alcohol. Alternatively, a 0.05 per cent solution in 0.1N sodium hydroxide may be used.

## Dry Test

*Blowpipe test.*—All magnesium compounds when ignited on charcoal in the presence of sodium carbonate are converted into white magnesium oxide, which glows brightly when hot. Upon moistening with a drop or two of cobalt nitrate solution and reheating strongly, a pale pink mass is obtained.

## POTASSIUM, K

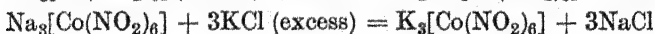
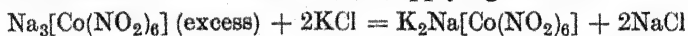
Potassium is a soft, silver-white metal. It remains unchanged in dry air, but is rapidly oxidised in moist air, becoming covered first with a blue film. The metal decomposes water violently, evolving hydrogen and burning with a violet flame. Potassium is usually kept under solvent naphtha. The salts are derived from the normal oxide  $K_2O$ .

\* For formula, see under Aluminium, Section III, 21, reaction 10.

### III, 34. REACTIONS OF THE POTASSIUM ION, $K^+$

Use a solution of potassium chloride,  $KCl$ .

1. **Sodium Cobaltinitrite Solution** ( $Na_3[Co(NO_2)_6]$ ): yellow precipitate of potassium-sodium cobaltinitrite  $K_2Na[Co(NO_2)_6]$ , insoluble in dilute acetic acid solution. The precipitate forms immediately in concentrated solutions and slowly in dilute solutions; precipitation may be accelerated by warming. Ammonium salts give a similar precipitate and must therefore be completely eliminated before applying the test. In alkaline solutions, a brown or black precipitate of cobaltic hydroxide  $Co(OH)_3$  is obtained. Iodides and other reducing agents interfere and should be removed before applying the test.



2. **Tartaric Acid Solution** ( $H_2.C_4H_4O_6$ )\*: white crystalline precipitate of potassium acid tartrate  $KH.C_4H_4O_6$  from concentrated solutions. The precipitate is slightly soluble in water (3.2 grams per litre; S.P.  $3.0 \times 10^{-4}$ ), insoluble in 50 per cent alcohol, soluble in mineral acids, and also in solutions of alkalis with the formation of the normal salts, e.g.  $K_2.C_4H_4O_6$ . Precipitation is accelerated by vigorous agitation of the solution, by scratching the sides of the vessel with a glass rod and by adding alcohol. Ammonium salts yield a similar precipitate and must be absent.



3. **Perchloric Acid Solution**† ( $HClO_4$ ): white crystalline precipitate of potassium perchlorate  $KClO_4$  from not too dilute solutions. The precipitate is slightly soluble in water (3.2 grams and 198 grams per litre at  $0^\circ$  and  $100^\circ$  respectively) and practically insoluble in absolute alcohol. *The alcoholic solution should not be heated as a dangerous explosion may result.* This reaction is unaffected by the presence of ammonium salts.



4. **Chloroplatinic Acid Solution** ( $H_2[PtCl_6]$ ): yellow crystalline precipitate of potassium chloroplatinate  $K_2[PtCl_6]$  from concentrated solutions; in dilute solutions, precipitation takes place slowly on standing, but may be hastened by cooling

\* Or preferably saturated sodium hydrogen tartrate solution.

† Twenty per cent strength. An equivalent result is obtained by the use of sodium perchlorate solution.

and by rubbing the sides of the vessel with a glass rod. The precipitate is slightly soluble in water, but is almost insoluble in 75 per cent alcohol. Ammonium salts give a similar precipitate and must be absent.



The reagent is prepared by dissolving 2.7 grams of the hydrated chloroplatinic acid  $\text{H}_2[\text{PtCl}_6] \cdot 6\text{H}_2\text{O}$  in 10 ml. of water. Owing to its expensive character, only small quantities should be employed and all precipitates placed in the platinum residues bottle.

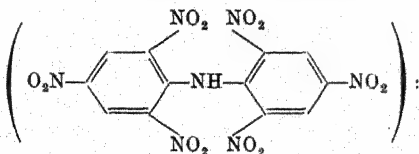
†5. **Sodium Cobaltinitrite-Silver Nitrate Test.**—This is a modification of reaction 1 and is applicable to halogen-free solutions. Precipitation of potassium salts with sodium cobaltinitrite and silver nitrate solution gives the compound  $\text{K}_2\text{Ag}[\text{Co}(\text{NO}_2)_6]$ , which is less soluble than the corresponding sodium compound  $\text{K}_2\text{Na}[\text{Co}(\text{NO}_2)_6]$  and hence the test is more sensitive. Lithium, thallium and ammonium salts must be absent for they give precipitates with sodium cobaltinitrite solution.

Place a drop of the neutral or acetic acid test solution on a black spot plate, and add a drop of 0.05 per cent silver nitrate solution and a small amount of finely-powdered sodium cobaltinitrite. A yellow precipitate or turbidity appears.

Sensitivity: 1  $\mu\text{g}$ . K. Concentration limit: 1 in 50,000.

If silver nitrate solution is not added, the sensitivity is 4  $\mu\text{g}$ . K.

†6. **Dipicrylamine (or Hexanitro-diphenylamine) Reagent**



the hydrogen atom of the NH group is replaceable by metals; the sodium salt is soluble in water to yield a yellow solution. With solutions of potassium salts, the latter gives a crystalline orange-red precipitate of the potassium derivative. The test is applicable in the presence of 80 times as much sodium and 130 times as much lithium. Ammonium salts should be removed before applying the test. Magnesium does not interfere.

Place a drop of the neutral test solution upon drop-reaction paper and immediately add a drop of the slightly alkaline reagent. An orange-red spot is obtained, which is unaffected by treatment with 1-2 drops of 2N hydrochloric acid.

Sensitivity: 3  $\mu\text{g}$ . K. Concentration limit: 1 in 10,000.

The reagent is prepared by dissolving 0.2 gram of dipicrylamine in 20 ml. of boiling 0.1N-sodium carbonate and filtering the cooled liquid.

## Dry Test

*Flame coloration.*—Potassium compounds, preferably the chloride, colour the non-luminous Bunsen flame violet (lilac). The yellow flame produced by small quantities of sodium obscures the violet colour, but by viewing the flame through two thicknesses of cobalt blue glass, the yellow sodium rays are absorbed and the reddish-violet potassium flame becomes visible. A solution of chrome alum (310 grams per litre), 3 cm. thick, also makes a good filter.

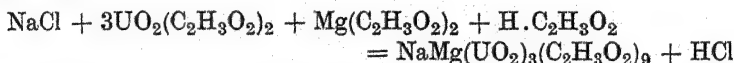
## SODIUM, Na

Sodium is a silver-white, soft metal. It oxidises rapidly in moist air and is therefore kept under solvent naphtha or xylene. The metal reacts violently with water forming sodium hydroxide and evolving hydrogen. The salts are derived from the monoxide  $\text{Na}_2\text{O}$ .

## III, 35. REACTIONS OF THE SODIUM ION, $\text{Na}^+$

Use a solution of sodium chloride,  $\text{NaCl}$ .

**1. Uranyl Magnesium Acetate Solution:** yellow, crystalline precipitate of sodium magnesium uranyl acetate  $\text{NaMg}(\text{UO}_2)_3(\text{C}_2\text{H}_3\text{O}_2)_9 \cdot 9\text{H}_2\text{O}$  from concentrated solutions. The addition of about one-third volume of alcohol helps the precipitation.



The reagent is prepared as follows. Dissolve 10 grams of uranyl acetate  $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$  in 6 grams of glacial acetic acid and 100 ml. of water (solution *a*). Dissolve 33 grams of magnesium acetate  $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$  in 10 grams of acetic acid and 100 ml. of water (solution *b*). Mix the two solutions *a* and *b*, allow to stand for 24 hours, and filter. Alternatively, a reagent of equivalent concentration may be prepared by dissolving uranyl magnesium acetate in the appropriate volume of water or of *N* acetic acid.

**2. Chloroplatinic Acid, Tartaric Acid or Sodium Cobaltinitrite Solution:** no precipitate with solutions of sodium salts.

**3. Uranyl Zinc Acetate Reagent.**—As a delicate test for sodium, the uranyl zinc acetate reagent is sometimes preferred to that employing uranyl magnesium acetate. The yellow crystalline sodium zinc uranyl acetate  $\text{NaZn}(\text{UO}_2)_3(\text{C}_2\text{H}_3\text{O}_2)_9 \cdot 9\text{H}_2\text{O}$  is obtained. The reaction is fairly selective for sodium.

The sensitivity of the reaction is affected by copper, mercury, cadmium, aluminium, cobalt, nickel, manganese, zinc, calcium, strontium, barium and ammonium when present in concentrations exceeding 5 grams per litre; potassium and lithium salts are precipitated if their concentration in solution exceeds 5 grams and 1 gram per litre respectively.

† Place a drop of the neutral test solution on a black spot plate or upon a black watch glass, add 8 drops of the reagent, and stir with a glass rod. A yellow cloudiness or precipitate forms.

Sensitivity: 12.5  $\mu\text{g}$ . Na. Concentration limit: 1 in 4,000.

The reagent is prepared as follows. Dissolve 10 grams of uranyl acetate in 6 grams of 30 per cent acetic acid, warming if necessary, and dilute with water to 50 ml. (solution *a*). In a separate vessel stir 30 grams of zinc acetate with 3 grams of 30 per cent acetic acid and dilute with water to 50 ml. (solution *b*). Mix the two solutions *a* and *b*, and add a small quantity of sodium chloride. Allow to stand for 24 hours, and filter from the precipitated sodium zinc uranyl acetate.

Alternatively, a reagent of equivalent concentration may be prepared by dissolving uranyl zinc acetate in the appropriate volume of water or of *N* acetic acid.

## Dry Test

*Flame coloration.*—The non-luminous Bunsen flame is coloured an intense yellow by vapours of sodium salts. The colour is not visible when viewed through two thicknesses of cobalt blue glass. Minute quantities of sodium salts give this test, and it is only when the colour is intense and persistent that appreciable quantities of sodium are present.

## III, 36. REACTIONS OF THE AMMONIUM ION, $\text{NH}_4^+$

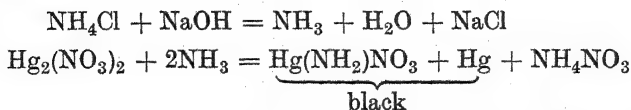
Use a solution of ammonium chloride,  $\text{NH}_4\text{Cl}$ .

1. **Sodium Hydroxide Solution:** ammonia gas is evolved on warming. This may be identified (*a*) by its odour (cautiously smell the vapour after removing the test-tube or small beaker from the flame); (*b*) by the formation of white fumes of ammonium chloride when a glass rod moistened with concentrated hydrochloric acid is held in the vapour; (*c*) by its turning moistened red litmus paper blue or turmeric paper brown; (*d*) by its ability to turn filter paper moistened with mercurous nitrate solution black (this is a very trustworthy test\*); and

\* Arsine, however, blackens mercurous nitrate paper, and must therefore be absent.



(e) filter paper moistened with a solution of manganous sulphate and hydrogen peroxide gives a brown colour, due to the oxidation of the manganese by the alkaline solution thus formed.



**2. Nessler's Reagent:** brown precipitate, or brown or yellow coloration, is produced according to the amount of ammonia or of ammonium ions. The test is an extremely delicate one and will detect the traces of ammonia present in drinking water. All metals, except those of the alkalis, must be absent.

The formula of the brown precipitate has been given as  $3\text{HgO} \cdot \text{Hg}(\text{NH}_3)_2\text{I}_2$  (Britton and Wilson, 1933) and as  $\text{NH}_2 \cdot \text{Hg}_2\text{I}_3$  (Nichols and Willits, 1934).

The reagent is prepared by dissolving 10 grams of potassium iodide in 10 ml. of ammonia-free water, adding saturated mercuric chloride solution (60 grams per litre) in small quantities at a time, with shaking, until a slight permanent precipitate is formed, then adding 80 ml. of 9*M* potassium hydroxide solution and diluting to 200 ml. Allow to stand overnight and decant the clear liquid. The reagent thus consists of an alkaline solution of potassium mercuri-iodide  $\text{K}_2[\text{HgI}_4]$ .

Nessler's reagent has been described as a solution which is *ca.* 0.09*M* in potassium mercuri-iodide and 2.5*N* in potassium hydroxide.

An alternative method for the preparation of the reagent is as follows. Dissolve 23 grams of mercuric iodide and 16 grams of potassium iodide in ammonia-free water and make up the volume to 100 ml.; add 100 ml. of 6*N* sodium hydroxide. Allow to stand for 24 hours, and decant the solution from any precipitate that may have formed. The solution should be kept in the dark.

† The spot-test technique is as follows. Mix a drop of the test solution with a drop of concentrated sodium hydroxide solution on a watch glass. Transfer a micro-drop of the resulting solution or suspension to drop reaction paper and add a drop of Nessler's reagent. A yellow or orange-red stain or ring is produced.

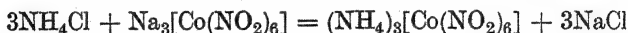
Sensitivity: 0.3  $\mu\text{g. NH}_3$  (in 0.002 ml.).

A better procedure is to employ the technique described under the manganous nitrate-silver nitrate reagent in reaction 9 below. A drop

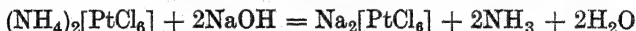
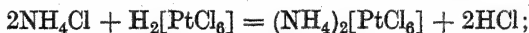
of Nessler's solution is placed on the glass knob of the apparatus. After the reaction is complete, the drop of the reagent is touched with a piece of drop reaction or quantitative filter paper when a yellow coloration will be apparent.

Sensitivity: 0.25  $\mu\text{g. NH}_3$ .

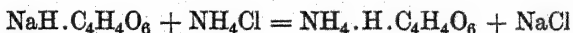
**3. Sodium Cobaltinitrite Solution** ( $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ ): yellow precipitate of ammonium cobaltinitrite  $(\text{NH}_4)_3[\text{Co}(\text{NO}_2)_6]$ , similar to that produced by potassium ions.



**4. Chloroplatinic Acid Solution** ( $\text{H}_2[\text{PtCl}_6]$ ): yellow, crystalline precipitate of ammonium chloroplatinate  $(\text{NH}_4)_2[\text{PtCl}_6]$ , similar to that of the corresponding potassium salt, but differing from it in being decomposed by warming with sodium hydroxide solution with the evolution of ammonia gas.



**5. Saturated Sodium Hydrogen Tartrate Solution** ( $\text{NaH.C}_4\text{H}_4\text{O}_6$ )\*: white precipitate of ammonium acid tartrate  $\text{NH}_4.\text{H.C}_4\text{H}_4\text{O}_6$ , similar to but slightly more soluble than the corresponding potassium salt, from which it is distinguished by the evolution of ammonia gas on being heated with sodium hydroxide solution.



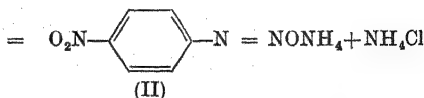
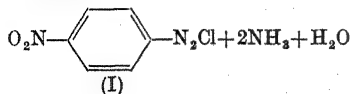
**6. Perchloric Acid or Sodium Perchlorate Solution:** no precipitate (distinction from potassium).

**7. Tannic Acid-Silver Nitrate Test.**—The basis of this test is the reducing action of tannic acid (a glucoside of digallic acid) upon the silver ammine complex  $[\text{Ag}(\text{NH}_3)_2]^+$  to yield black silver: it therefore precipitates silver in the presence of ammonia but not from a slightly acid silver nitrate solution.

Mix 2 drops of 5 per cent tannic acid (tannin) solution with 2 drops of 20 per cent silver nitrate solution, and place the mixture upon drop-reaction paper or upon a little cotton wool. Hold the paper in the vapour produced by heating an ammonium salt with sodium hydroxide solution. A black stain is formed on the paper or upon the cotton wool. The test is a sensitive one.

\* Or, less effectively, tartaric acid solution.

†8. **para-Nitrobenzene-diazonium Chloride Reagent.**—The reagent (I) yields a red coloration (due to II) with an ammonium salt in the presence of sodium hydroxide solution.



Place a drop of the neutral or slightly acid test solution on a spot plate, followed by a drop of the reagent and a fine granule of calcium oxide between the two drops. A red zone forms round the calcium oxide. A blank test should be carried out on a drop of water.

Sensitivity: 0.7  $\mu\text{g}$ . Concentration limit: 1 in 75,000.

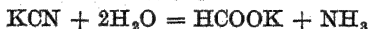
The reagent (sometimes known as Riegler's solution) is prepared as follows. Dissolve 1 gram of *p*-nitraniline in 2 ml. of concentrated hydrochloric acid and 20 ml. of distilled water (warming may be necessary) and dilute with 160 ml. of water. Cool, add 20 ml. of 2–5 per cent sodium nitrite solution with vigorous shaking. Continue the shaking until all dissolves. The reagent becomes turbid on keeping, but can be employed again after filtering.

†9. **Ammonia-Formation Test.**—This is a modification of reaction 1 as adapted to delicate analysis. The apparatus is shown in Fig. II, 6, 12 and consists of a small glass tube of 1 ml. capacity, which can be closed with a small ground-glass stopper carrying a small glass hook at the lower end.

Place a drop of the test solution or a little of the solid in the micro test-tube, and add a drop of 2*N* sodium hydroxide solution. Fix a small piece of red litmus paper on the glass hook and insert the stopper into position. Warm to 40°C for 5 minutes. The paper assumes a blue colour.

Sensitivity: 0.01  $\mu\text{g}$ . $\text{NH}_3$ . Concentration limit: 1 in 5,000,000.

Cyanides should be absent, for they give ammonia with alkalis:



If, however, a little mercuric oxide or a mercuric salt is added, the alkali-stable mercuric cyanide  $\text{Hg}(\text{CN})_2$  is formed and the interfering effect of cyanides is largely eliminated.

An alternative method for carrying out the test is to employ the **manganous nitrate-silver nitrate reagent**. Upon treating a neutral solution of manganous and silver salts with alkalis (*e.g.* that produced from ammonia), a black precipitate is formed:



The sensitivity can be increased by treating the resultant precipitate with an acetic acid solution of benzidine whereupon the manganese dioxide oxidises the benzidine to a blue oxidation product.

Use the apparatus shown in Fig. II, 6, 10 or in Fig. II, 6, 11. Place a drop of the test solution and a drop of 2*N* sodium hydroxide in the

micro test-tube; also place a drop of the reagent on the glass knob of the stopper and close the apparatus. Heat at  $40^{\circ}\text{C}$  for 5 minutes. Wash the drop of the reagent on to a piece of quantitative filter paper when a black or grey fleck will become apparent; this turns blue upon treatment with a solution of benzidine (the latter is prepared by dissolving 0.05 gram of benzidine or its hydrochloride in 10 ml. of glacial acetic acid, diluting to 100 ml. with water, and filtering).

Sensitivity:  $0.005\ \mu\text{g. NH}_3$ . Concentration limit: 1 in 10,000,000.

The **manganous nitrate-silver nitrate reagent** is prepared thus. Dissolve 2.87 grams of manganous nitrate in 40 ml. of water, and filter: add a solution of 3.55 grams of silver nitrate in 40 ml. of water, and dilute the mixture to 100 ml. Neutralise the acid formed by hydrolysis by adding dilute alkali dropwise until a black precipitate is formed and filter. Keep the reagent in a dark bottle.

## Dry Test

All ammonium salts are either volatilised or decomposed when heated to just below red heat. In some cases, where the acid is volatile, the vapours recombine on cooling to form a sublimate of the salt, *e.g.* ammonium chloride.

## DETECTION AND SEPARATION OF THE METALS OF THE ALKALI GROUP (GROUP V)

The metals of this group are not precipitated by the earlier group reagents. It is assumed that the elements of Groups I to IV have been removed as already described, or that only metals of Group V are present. The student should, as in previous groups, prepare for himself or obtain from the teacher, a solution containing some or all of the simple salts of the metals of the group. The filtrate from Group IV, if employed, should be evaporated to dryness and all ammonium salts eliminated. This is most conveniently carried out by concentrating the solution in an evaporating dish (FUME CUPBOARD!) until salts begin to crystallise out, allowing to cool, then adding a little concentrated nitric acid by means of a dropper pipette in such a manner as to wash down the solid from the sides to the centre of the dish, then heating cautiously until dry and finally more strongly until fuming ceases. The cold residue may then be divided into two portions: one is used in testing for Mg with the "oxine" reagent, and the other in testing for Na and K and also for the confirmatory test for Mg.

The sodium phosphate test for Mg (see Section III, 33, reaction 5) is not altogether satisfactory, particularly in dilute solutions when precipitation is comparatively slow, and also the magnesium ammonium phosphate has a tendency to form supersaturated solutions; traces of alkaline earth metals tend to interfere with the test.

## III, 37. Table VII. Analysis of the Alkali Group (Group V)

Treat the dry residue from Group IV with 3-4 ml. of water, stir and warm for 1 minute. Filter.\*

**Residue.** Dissolve in a few drops of dilute HCl and add 2-3 ml. of water. Divide the solution into two unequal parts.

(i) *Larger portion* (1). Treat 1 ml. of 2% oxine solution in 2N acetic acid with 4 ml. of 2.5N ammonia solution and, if necessary, warm to dissolve any precipitated oxine. Add a little  $\text{NH}_4\text{Cl}$  solution to the test solution, followed by the ammoniacal oxine reagent, and heat to the boiling point for 1-2 minutes (the odour of  $\text{NH}_3$  should be discernible). Pale yellow ppt. of Mg "oxinate."

**Mg present.**

(ii) *Smaller portion.* To 3-4 drops add 2 drops of "magneson" reagent, followed by several drops of NaOH solution until alkaline.

A blue ppt. confirms Mg.

**Filtrate.** Divide the filtrate into two parts (a) and (b).

(a) Add a little uranyl magnesium acetate reagent, shake and allow to stand for a few minutes.

Yellow crystalline ppt.

**Na present.**

Confirm by flame test: *persistent* yellow flame.

(b) Add a little sodium cobalt-nitrite solution and a few drops of dilute acetic acid, preferably on a watch glass.

Yellow ppt. of  $\text{K}_3[\text{Co}(\text{NO}_2)_6]$ .

**K present.**

Confirm by flame test and view through two thicknesses of cobalt glass (2): red coloration (usually transient).

*Test for ammonium* by boiling the original substance with sodium hydroxide solution: odour of ammonia, and vapour turns red litmus paper blue and also mercurous nitrate paper black. **Ammonium present.**

**Notes.** (1) If it is desired to carry out the  $\text{Na}_2\text{HPO}_4$  test for comparison with the "oxine" test for Mg, treat the acid solution with a little  $\text{NH}_4\text{Cl}$ , followed by dilute  $\text{NH}_3$  solution until basic, and  $\text{Na}_2\text{HPO}_4$  solution. Shake or stir vigorously. A white crystalline ppt. of  $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$  indicates Mg. Confirm by dissolving the ppt. in a little dilute HCl and then applying the "magneson" test. A blue ppt. confirms Mg.

(2) It is advisable to test the cobalt glass with a potassium salt to be certain that the glass is satisfactory: some samples of cobalt glass completely absorb the red lines due to potassium.

\* If the residue dissolves completely (or almost completely) in water, dilute the resulting solution (after filtration, if necessary) to about 6 ml. and divide it into three approximately equal parts:— (i) Use the major portion to test for Mg with the prepared "oxine" solution: confirm Mg by applying the "magneson" test to 3-4 drops of the solution; (ii) and (iii) Test for Na and K respectively, as described in the Table.

### III, 37. Table SMVII. Analysis of the Alkali Group (Group V)

Treat the dry residue (contained in a small crucible) from Group IV with 1 ml. of water, stir for 1 minute, and transfer with the aid of a further 0.5 ml. of water to a semimicro centrifuge tube. Centrifuge.\*

**Residue.** Dissolve in a few drops of dilute HCl, and add 1 ml. of water. Divide into two unequal parts; retain the smaller portion in the centrifuge tube.

(i) *Larger portion* (1). Treat 0.25 ml. of 2% oxine solution in 2N acetic acid with 1 ml. of 2.5N ammonia solution. Add a little  $\text{NH}_4\text{Cl}$  to the test solution followed by the ammoniacal oxine reagent, and heat in a water bath for 1–2 minutes (the odour of  $\text{NH}_3$  should be apparent).

Pale yellow ppt. of Mg "oxinate."

**Mg present.**

(ii) *Smaller portion.* To 3–4 drops add 2 drops of "magneson" reagent, followed by several drops of NaOH solution until alkaline.

A blue ppt. confirms Mg.

**Centrifugate.** Divide into two parts (a) and (b).

(a) Add 5–10 drops of uranyl magnesium acetate reagent, shake or stir, and allow to stand for 5 minutes.

Yellow crystalline ppt.

**Na present.**

Confirm by flame test: *persistent* yellow flame.

(b) Add 3 drops of sodium cobaltinitrite reagent (or 5 mg. of the A.R. solid) and 2 drops of dilute acetic acid, warm gently on water bath, and allow to stand for 3 minutes.

Yellow ppt. of  $\text{K}_3[\text{Co}(\text{NO}_2)_6]$ .

**K present.**

Confirm by flame test and view through two thicknesses of cobalt glass (2): red (crimson) flame (usually transient).

*Test for ammonium* by placing 10 mg. of the original substance with about 0.5 ml. of sodium hydroxide solution in a semimicro test-tube (without rim) and attach a "filter tube" (Fig. II, 3, 19). Place a piece of red litmus paper or mercurous nitrate paper in the funnel. Warm on a water bath. Odour of ammonia: red litmus paper turns blue; mercurous nitrate paper turns black. **Ammonium present.**

**Notes.** (1) If it is desired to carry out the  $\text{Na}_2\text{HPO}_4$  test for comparison with the "oxine" test for Mg, treat the acid solution with a little  $\text{NH}_4\text{Cl}$ , followed by dilute  $\text{NH}_3$  solution until alkaline, and 5–6 drops of  $\text{Na}_2\text{HPO}_4$  solution. Shake or stir the mixture and allow to stand for 3–5 minutes. A white crystalline ppt. of  $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$  indicates Mg. Centrifuge and wash the ppt. with 0.3 ml. of water: discard the washings. Dissolve the ppt. in 5 drops of dilute HCl, warming if necessary. Add 1 drop of the "magneson" reagent, and then NaOH solution until alkaline. A blue ppt. confirms Mg.

(2) See Note 2 in macro Table VII.

\* If the residue dissolves completely (or almost completely) in water, dilute the resulting solution (after centrifugation, if necessary) to about 1.5 ml. and divide it into three approximately equal parts:— (i) Use the major portion to test for Mg with the prepared "oxine" solution; confirm Mg by applying the "magneson" test to 3–4 drops of the solution; (ii) and (iii) Test for Na and K respectively, as described in the Table.

## CHAPTER IV

### REACTIONS OF THE ACID RADICALS OR ANIONS

**IV, 1. Scheme of Classification.**—The methods available for the detection of acid radicals or anions are not as systematic as those which have been described in the previous chapter for cations. No really satisfactory scheme has yet been proposed which permits of the separation of the common acid radicals into major groups, and the subsequent unequivocal separation of each group into its independent constituents. It must, however, be mentioned that it is possible to separate the anions into major groups dependent upon the solubilities of the silver salts, of the calcium or barium salts, and of the zinc salts; these, however, can only be regarded as useful in giving an indication of the limitations of the method and for the confirmation of the results obtained by the simpler procedures to be described below. For this reason their discussion is deferred until Section VII, 16 in connexion with the complete systematic detection of acid radicals.

The following *scheme of classification* has been found to work well in practice; it is not a rigid one since some of the acid radicals belong to more than one of the subdivisions, and, furthermore, it has no theoretical basis. Essentially the processes employed may be divided into (A) those involving the identification by volatile products obtained on treatment with acids, and (B) those dependent upon reactions in solution. Class (A) is subdivided into (i) gases evolved with dilute hydrochloric acid or dilute sulphuric acid, and (ii) gases or vapours evolved with concentrated sulphuric acid. Class (B) is subdivided into (i) precipitation reactions, and (ii) oxidation and reduction in solution.

This leads to the following classification.

#### CLASS A

(i) *Gases evolved with dilute hydrochloric acid or dilute sulphuric acid.*

Carbonate, bicarbonate, sulphite, thiosulphate, sulphide, nitrite, hypochlorite, cyanide and cyanate.

(ii) *Gases or acid vapours evolved with concentrated sulphuric acid.*

These include those of (i) with the addition of the following: fluoride, silicofluoride,\* chloride, bromide, iodide, nitrate, chlorate (*DANGER*), perchlorate, permanganate (*DANGER*), bromate, borate,\* ferrocyanide, ferricyanide, thiocyanate, formate, acetate, oxalate, tartrate and citrate.

### CLASS B

#### (i) *Precipitation reactions.*

Sulphate, persulphate,† phosphate, phosphite, hypophosphite, arsenate, arsenite, chromate, dichromate, silicate, silicofluoride, salicylate, benzoate and succinate.

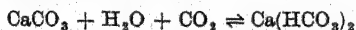
#### (ii) *Oxidation and reduction in solution.*

Manganate, permanganate, chromate and dichromate.

The reactions of all these acid radicals or anions will be systematically studied in the following pages. For convenience the reactions of certain organic acids are grouped together; these include acetates, formates, oxalates, tartrates, citrates, salicylates, benzoates and succinates. It may be pointed out that acetates, formates, salicylates, benzoates and succinates all belong to another group; all give a characteristic coloration or precipitate upon the addition of ferric chloride solution to a practically neutral solution.

## IV, 2. REACTIONS OF CARBONATES, $\text{CO}_3^{--}$

*Solubility.*—All normal carbonates, with the exception of those of the alkali metals and of ammonium, are insoluble in water. The acid carbonates or bicarbonates of calcium, strontium, barium, magnesium and possibly of iron exist in aqueous solution; they are formed by the action of excess of carbonic acid upon the normal carbonates either in aqueous solution or suspension and are decomposed on boiling the solutions.



The bicarbonates of the alkali metals are soluble in water, but are less soluble than the corresponding normal carbonates.

Use sodium carbonate,  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ .

**1. Dilute Hydrochloric Acid†:** decomposition with effervescence, due to the evolution of carbon dioxide, which may be detected by its property of rendering lime water (or baryta water) turbid. Some natural carbonates, such as magnesite  $\text{MgCO}_3$ , siderite  $\text{FeCO}_3$  and dolomite  $(\text{Ca}, \text{Mg})\text{CO}_3$ , do not

\* This is often included in Class B (i).

† Strictly speaking persulphates should be grouped with Class B (ii), but are best studied together with sulphates.

‡ Or any other dilute mineral acid.



react appreciably in the cold; they must be finely powdered and the reaction mixture warmed.

The lime water or baryta water test is best carried out in the apparatus shown in Fig. IV, 2, 1. The solid substance is placed in the test-tube or small distilling flask (10–25 ml. capacity), dilute hydrochloric acid added and the cork immediately replaced. The gas which is evolved (warming may be necessary) is passed into lime water or baryta water contained in the test-tube; the production of a turbidity indicates the presence of a carbonate. It must be remembered that with prolonged passage of carbon dioxide, the turbidity slowly disappears as a result of the formation of a soluble bicarbonate. Any acid which is "stronger," i.e. has a higher

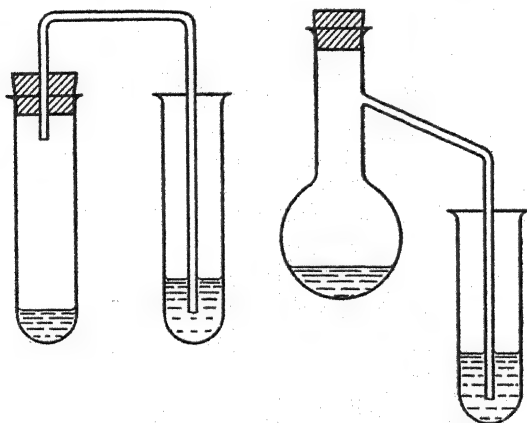
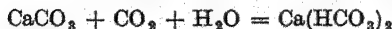
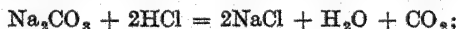


Fig. IV, 2, 1.

ionisation constant, than carbonic acid ( $K_1$ ) will displace it from its salts, especially on warming. The weak hydrocyanic acid, boric acid and hydrogen sulphide do not decompose carbonates.



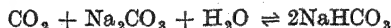
**2. Barium Chloride or Calcium Chloride Solution:** white precipitate of barium carbonate  $\text{BaCO}_3$  or calcium carbonate  $\text{CaCO}_3$  with solutions of *normal* carbonates. The precipitate is soluble in mineral acids and in carbonic acid.



**3. Silver Nitrate Solution:** white precipitate of silver carbonate  $\text{Ag}_2\text{CO}_3$  with solutions of normal carbonates, soluble

in ammonia solution and in nitric acid. The precipitate becomes yellow upon addition of excess of the reagent, and is partly decomposed on boiling with water into brown silver oxide  $\text{Ag}_2\text{O}$  and carbon dioxide.

†4. **Sodium Carbonate-Phenolphthalein Test.**—This test depends upon the fact that phenolphthalein is turned pink by soluble carbonates and colourless by soluble bicarbonates. Hence if the carbon dioxide liberated by dilute acids from carbonates is allowed to come into contact with phenolphthalein solution coloured pink by sodium carbonate solution, it may be identified by the decolourisation which takes place:



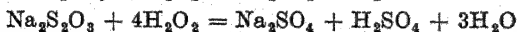
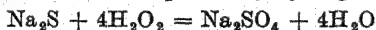
The concentration of the sodium carbonate solution must be such as not to be decolourised under the conditions of the experiment by the carbon dioxide in the atmosphere.

Place 1–2 drops of the test solution (or a small quantity of the test solid) in the apparatus shown in Fig. II, 6, 10, and place a drop of the sodium carbonate-phenolphthalein reagent on the knob of the stopper. Add 3–4 drops of 2N sulphuric acid and insert the stopper into position. The drop is decolourised either immediately or after a short time according to the quantity of carbon dioxide formed. Perform a blank test in a similar apparatus.

Sensitivity:  $4 \mu\text{g. CO}_2$  (in 2 drops of solution). Concentration limit: 1 in 12,500.

The reagent is prepared by mixing 1 ml. of 0.1N sodium carbonate with 2 ml. of a 0.5 per cent solution of phenolphthalein and 10 ml. of water.

Sulphides, sulphites, thiosulphates, cyanides, cyanates, fluorides, nitrites and acetates interfere. The sulphur-containing anions can be quantitatively oxidised to sulphates by hydrogen peroxide:

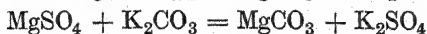
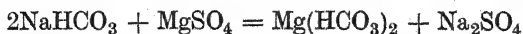


The modified procedure in the presence of these anions is therefore to stir a drop of the test solution with 2 drops of "20–40 volume" hydrogen peroxide, then to add 2 drops of 2N sulphuric acid, and to continue as above. Cyanides are rendered innocuous by treating the test solution with 4 drops of a saturated solution of mercuric chloride, followed by 2 drops of sulphuric acid, etc.; the slightly dissociated mercuric cyanide is formed. Nitrites can be removed by treatment with aniline hydrochloride.

**IV, 3. Tests for bicarbonates.**—The following tests distinguish carbonates from bicarbonates.

(i) To a cold solution of a bicarbonate, *e.g.* sodium bicarbonate  $\text{NaHCO}_3$ , add a solution of magnesium sulphate. No precipitate is formed in the cold since magnesium bicarbonate  $\text{Mg}(\text{HCO}_3)_2$  is soluble in water. Boil the solution: a white precipitate of magnesium carbonate  $\text{MgCO}_3$ , which

may be contaminated with some of the basic carbonate, is produced. Solutions of carbonates give a white precipitate of magnesium carbonate with magnesium sulphate solution in the cold.

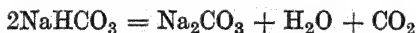


(ii) Boil a solution of a bicarbonate. Carbon dioxide is evolved which may be identified by the lime water test.

(iii) Add mercuric chloride solution to a solution of a bicarbonate. No precipitate is formed. Normal carbonates yield a reddish-brown precipitate of basic carbonate  $\text{Hg}_4\text{O}_3 \cdot \text{CO}_3$  in the cold.



(iv) Heat some solid sodium bicarbonate in a dry test-tube; carbon dioxide is evolved. The residue evolves carbon dioxide upon treatment with dilute mineral acid.



(v) To test for bicarbonate in the presence of a carbonate, use is made of the fact that calcium bicarbonate  $\text{Ca}(\text{HCO}_3)_2$  is soluble in water and is converted into calcium carbonate  $\text{CaCO}_3$  by the addition of ammonia solution. Add excess of calcium chloride solution; this will precipitate all the carbonate and part of the bicarbonate as  $\text{CaCO}_3$ . After a few minutes, filter rapidly and treat the clear filtrate with a little ammonia solution. A white precipitate or cloudiness is obtained if a bicarbonate is present.

#### IV, 4. REACTIONS OF SULPHITES, $\text{SO}_3^-$

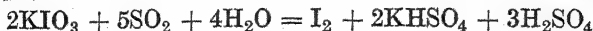
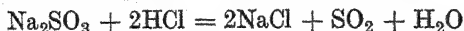
*Solubility.*—Only the sulphites of the alkali metals and of ammonium are soluble in water; the sulphites of the other metals are either difficultly soluble or insoluble in water. The bisulphites of the alkali metals are soluble in water; the bisulphites of the alkaline earth metals are known only in solution.

Use sodium sulphite,  $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ .\*

1. Dilute Hydrochloric or Dilute Sulphuric Acid: the solid salt is decomposed, more rapidly on warming, with the evolution of sulphur dioxide, which may be identified (i) by its suffocating odour of burning sulphur, (ii) by the green coloration produced when filter paper moistened with acidified potassium dichromate solution is held over the mouth of the test-tube, and (iii) by the blue colour produced when filter

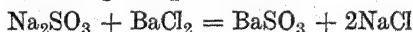
\* Unless otherwise indicated, in this and all subsequent Sections concerned with anions, the aqueous solutions should be employed.

paper moistened with potassium iodate solution and starch solution is held in the vapour.

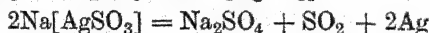
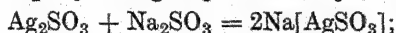
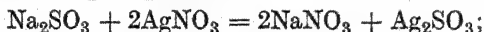


## 2. Barium Chloride or Strontium Chloride Solution:

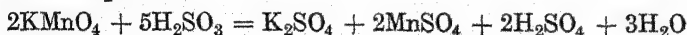
white precipitate of the sulphite  $\text{BaSO}_3$  or  $\text{SrSO}_3$ , readily soluble in dilute hydrochloric acid. On standing, the precipitate is slowly oxidised to the sulphate and is then insoluble in dilute mineral acids; this change is rapidly effected by warming with bromine water or a little concentrated nitric acid or with hydrogen peroxide. The solubilities at  $18^\circ$  of the sulphites of calcium, strontium and barium are respectively 1.25 grams, 0.033 gram and 0.022 gram per litre.



3. **Silver Nitrate Solution:** white crystalline precipitate of silver sulphite  $\text{Ag}_2\text{SO}_3$ , soluble in excess of the sulphite solution forming the complex salt, sodium argenti-sulphite  $\text{Na}[\text{AgSO}_3]$ . The precipitate is also soluble in ammonia solution and in dilute nitric acid. On boiling a solution of the complex salt or an aqueous suspension of the precipitate, grey metallic silver is precipitated.

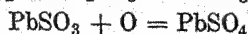
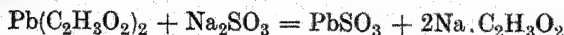


4. **Potassium Permanganate Solution\*:** decolourised owing to the formation of solutions of potassium and manganese sulphates.



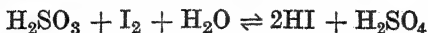
5. **Potassium Dichromate Solution\*:** a green solution containing a chromic salt is produced. (Equation under reaction 1.)

6. **Lead Acetate Solution:** white precipitate of lead sulphite  $\text{PbSO}_3$ , readily soluble in cold dilute nitric acid, and precipitating white lead sulphate on boiling (distinction from thiosulphate).

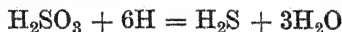


\* Acidified with dilute sulphuric acid.

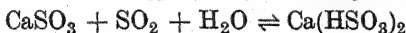
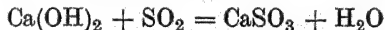
## 7. Iodine Solution: decolourised.



8. **Nascent Hydrogen.**—Add the solution of the sulphite to a test-tube containing zinc and dilute sulphuric acid; hydrogen sulphide is evolved which may be detected by holding some lead acetate paper at the mouth of the test-tube (see Section IV, 6, reaction 1).



9. **Lime Water.**—This test is carried out by adding dilute hydrochloric acid to the solid sulphite, and bubbling the evolved sulphur dioxide through lime water (Fig. IV, 2, 1); a white precipitate of calcium sulphite  $\text{CaSO}_3$  is formed. The precipitate dissolves on prolonged passage of the gas, due to the formation of the soluble calcium bisulphite  $\text{Ca}(\text{HSO}_3)_2$ . A turbidity is also produced by carbonates; the sulphur dioxide must therefore be first removed when testing for the latter. This may be effected by adding potassium dichromate solution to the test-tube before acidifying. The dichromate oxidises and destroys the sulphur dioxide without affecting the carbon dioxide (compare Section IV, 2).



†10. **Fuchsin Test.**—Dilute solutions of triphenylmethane dyestuffs, such as fuchsin (for formula, see Section IV, 15, reaction 9) and malachite green, are immediately decolourised by neutral sulphites. Sulphur dioxide also decolourises fuchsin solution, but the reaction is not quite complete: nevertheless it is a very useful test for sulphurous acid and acid sulphites; carbon dioxide does not interfere, but nitrogen dioxide does. If the test solution is acid, it should preferably be just neutralised with sodium bicarbonate. Thiosulphates do not interfere but sulphides, polysulphides and free alkali do. Zinc, lead and cadmium salts reduce the sensitivity of the test, hence the interference of sulphides cannot be obviated by the addition of these salts.

Place 1 drop of the fuchsin reagent on a spot plate and add 1 drop of the neutral test solution. The reagent is decolourised.

Sensitivity:  $1 \mu\text{g. SO}_2$ . Concentration limit: 1 in 50,000.

The fuchsin reagent is prepared by dissolving 0.015 gram of fuchsin in 100 ml. of water.

†11. **Nickelous Hydroxide Test.**—The auto-oxidation of sulphur dioxide (or sulphurous acid) induces the oxidation of green nickelous hydroxide to the black nickelic hydroxide. The colour change is quite distinct, but for very small amounts of sulphur dioxide use may be made of the conversion of benzidine acetate to "benzidine blue" by the higher nickel oxide. Thiosulphates give a similar reaction and must therefore be absent: sulphides also interfere.

Place a drop of the test solution (or a little of the test solid) in the tube of the apparatus shown in Fig. II, 6, 10, and place a little washed nickelous hydroxide on the glass knob under the stopper. Add 1-2 drops of 5-6*N* hydrochloric acid, close the apparatus and warm gently. The green hydroxide turns grey to black according to the amount of sulphite present. For small amounts of sulphites, transfer the nickel hydroxide to a quantitative filter paper and treat with a drop of the benzidine reagent: a blue colour is formed.

An alternative technique is to warm (water bath) the test solution in a semimicro test-tube with a little dilute hydrochloric acid, and expose the evolved gas to filter paper upon which a stain of nickelous hydroxide has been made. The stain acquires a black colour.

Sensitivity: 0.4  $\mu\text{g. SO}_2$ . Concentration limit: 1 in 125,000.

The **nickelous hydroxide** is prepared by precipitating nickelous chloride solution with sodium hydroxide solution and washing thoroughly until free from alkali. It should be freshly prepared.

The **benzidine reagent** is prepared by dissolving 0.05 gram of benzidine or of its hydrochloride in 10 ml. of glacial acetic acid, diluting to 100 ml. with water and filtering.

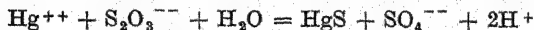
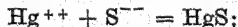
†12. **Sodium Nitroprusside-Zinc Sulphate Test.**—Sodium nitroprusside solution reacts with a solution of a zinc salt to yield a salmon-coloured precipitate of zinc nitroprusside  $\text{Zn}[\text{Fe}(\text{CN})_5\text{NO}]$ . The latter reacts with moist sulphur dioxide to give a red compound of unknown composition; the test is rendered more sensitive when the reaction product is held over ammonia vapour which decolourises the unused zinc nitroprusside.

Place a drop of the test solution (or a grain of the solid test sample) in the tube of Fig. II, 6, 10 and coat the knob of the glass stopper with a thin layer of the zinc nitroprusside paste. Add a drop of 2*N* hydrochloric or sulphuric acid and close the apparatus. After the sulphur dioxide has been evolved, hold the stopper for a short time in ammonia vapour. The paste is coloured more or less deep red.

Sensitivity: 3.5  $\mu\text{g. SO}_2$ . Concentration limit: 1 in 14,000.

The **zinc nitroprusside paste** is prepared by precipitating sodium nitroprusside solution with an excess of zinc sulphate solution and boiling for a few minutes: the precipitate is filtered and washed, and kept in a dark glass bottle or tube.

The test is not applicable in the presence of sulphides and/or thio-sulphates. These can be removed by the addition of mercuric chloride, which reacts forming the acid-stable mercuric sulphide:



Place a drop of the test solution and 2 drops of saturated mercuric chloride solution in the same apparatus (Fig. II, 6, 10) and, after a minute, acidify with 2*N* hydrochloric or sulphuric acid, and proceed as above.

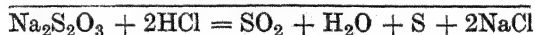
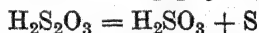
20  $\mu\text{g. of Na}_2\text{SO}_3$  can be detected in the presence of 900  $\mu\text{g. of Na}_2\text{S}_2\text{O}_3$  and 1,500  $\mu\text{g. of Na}_2\text{S}$ .

IV, 5. REACTIONS OF THIOSULPHATES,  $S_2O_3^{--}$ 

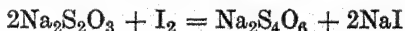
*Solubility.*—Most of the thiosulphates that have been prepared are soluble in water; those of lead, silver and barium are very sparingly soluble. Many of them dissolve in an excess of sodium thiosulphate solution forming complex salts.

Use sodium thiosulphate,  $Na_2S_2O_3 \cdot 5H_2O$ .

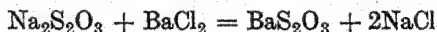
**1. Dilute Hydrochloric Acid:** no immediate change in the cold with a solution of a thiosulphate; the acidified liquid soon becomes turbid owing to the separation of sulphur, and sulphurous acid is present in solution. On warming the solution, sulphur dioxide is evolved which is recognised by its odour and its action upon filter paper moistened with acidified potassium dichromate solution. The unstable thiosulphuric acid is first formed; this soon decomposes largely into sulphurous acid and sulphur. The sulphur first forms a colloidal solution, which is gradually coagulated by the free acid present. Side reactions also occur giving rise to thionic acids.



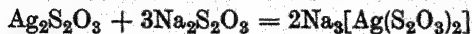
**2. Iodine Solution:** decolourised; a colourless solution of sodium tetrathionate  $Na_2S_4O_6$  is formed.



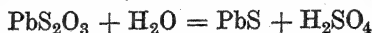
**3. Barium Chloride Solution:** white precipitate of barium thiosulphate  $BaS_2O_3$  from moderately concentrated solutions. Precipitation is accelerated by agitation and by rubbing the sides of the vessel with a glass rod. The solubility is 0.5 gram per litre at  $18^\circ$ . No precipitate is obtained with calcium chloride solution since calcium thiosulphate is fairly soluble in water.



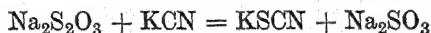
**4. Silver Nitrate Solution:** white precipitate of silver thiosulphate  $Ag_2S_2O_3$ , readily soluble in excess of the thiosulphate solution forming the complex salt  $Na_3[Ag(S_2O_3)_2]$ . The precipitate is unstable, decomposing on standing and rapidly on warming; the colour changes through yellow and brown to black silver sulphide  $Ag_2S$ .



**5. Lead Acetate Solution:** white precipitate of lead thiosulphate  $\text{PbS}_2\text{O}_3$ , soluble in excess of the precipitant; on boiling the suspension, a black precipitate containing lead sulphide  $\text{PbS}$  is obtained (distinction from sulphite).



**6. Potassium Cyanide Solution.**—A thiocyanate is produced when a solution of a thiosulphate is boiled with solutions of potassium cyanide and sodium hydroxide. On acidifying with dilute hydrochloric acid and adding ferric chloride solution, the characteristic blood-red colour of the complex ferri-thiocyanate ion  $[\text{Fe}(\text{SCN})]^{++}$  is obtained (distinction from sulphite).



**7. "Blue Ring" Test.**—When a solution of a thiosulphate mixed with ammonium molybdate solution is poured *slowly* down the side of a test-tube containing concentrated sulphuric acid, a blue ring is formed at the contact zone.

**8. Ferric Chloride Solution:** dark violet coloration (perhaps due to sodium ferri-thiosulphate,  $\text{Na}[\text{Fe}(\text{S}_2\text{O}_3)_2]$ ) which disappears after a short time leaving an almost colourless solution.



### 9. Nickel Ethylenediamine Nitrate Reagent

$[\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3](\text{NO}_3)_2$ , abbreviated to  $[\text{Ni en}_3](\text{NO}_3)_2$ .—

When a neutral or slightly alkaline solution of a thiosulphate is treated with the reagent, a crystalline violet precipitate of the complex thiosulphate is obtained:



Sulphites, sulphates, tetrathionates and thiocyanates do not interfere, but hydrogen sulphide and ammonium sulphide decompose the reagent with the precipitation of nickel sulphide.

The **nickel ethylenediamine nitrate reagent** is conveniently prepared when required by treating a little nickel nitrate solution with ethylenediamine until a violet colour (due to the formation of the complex  $[\text{Ni en}_3]^{++}$  ion) appears.

The concentration limit is 1 in 25,000.

By obvious modification the reaction may be used for the detection of nickel; it is applicable in the presence of copper, cobalt, iron and chromium.

†**10. Catalysis of Iodine-Azide Reaction Test.**—Solutions of sodium azide  $\text{NaN}_3$  and of iodine (as  $\text{KI}_2$ ) do not react, but on the



addition of a trace of thiosulphate, which acts as a catalyst, there is an immediate vigorous evolution of nitrogen:



Sulphides and thiocyanates act similarly and must therefore be absent.

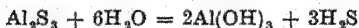
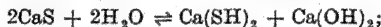
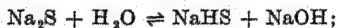
Mix a drop of the test solution and a drop of the iodine-azide reagent on a watch glass. A vigorous evolution of bubbles (nitrogen) ensues.

Sensitivity: 0.15  $\mu\text{g}$ .  $\text{Na}_2\text{S}_2\text{O}_3$ . Concentration limit: 1 in 330,000.

The sodium azide-iodine reagent consists of a solution of 3 grams of sodium azide in 100 ml. of 0.1*N* iodine.

#### IV, 6. REACTIONS OF SULPHIDES, $\text{S}^{--}$

*Solubility.*—The acid, normal and poly-sulphides of the alkali metals are soluble in water; their aqueous solutions react alkaline because of hydrolysis. The normal sulphides of most other metals are insoluble; those of the alkaline earths are difficultly soluble, but are gradually changed by contact with water into soluble hydrosulphides. The sulphides of aluminium, chromium and magnesium are completely hydrolysed by water, and can be prepared only by dry methods. The characteristic colours and solubilities of many metallic sulphides have already been discussed in connexion with the reactions of the cations in Chapter III. The sulphides of iron, manganese, zinc and the alkali metals are decomposed by dilute hydrochloric acid with the evolution of hydrogen sulphide; those of lead, cadmium, nickel, cobalt, antimony and stannic tin require concentrated hydrochloric acid for decomposition; others, such as mercuric sulphide, are insoluble in concentrated hydrochloric acid, but dissolve in aqua regia with the separation of sulphur. The presence of sulphide in insoluble sulphides may be detected by reduction with nascent hydrogen (derived from zinc or tin and hydrochloric acid) to the metal and hydrogen sulphide, the latter being identified with lead acetate paper (see reaction 1 below). An alternative method is to fuse the sulphide with anhydrous sodium carbonate, extract the mass with water and to treat the filtered solution with freshly prepared sodium nitroprusside solution, when a purple colour will be obtained: the sodium carbonate solution may also be treated with lead nitrate solution when black lead sulphide is precipitated.

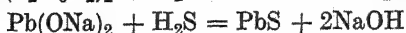
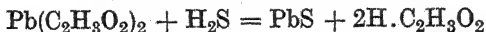


Use sodium sulphide,  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ .

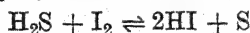
**1. Dilute Hydrochloric Acid\*:** hydrogen sulphide gas is evolved, which may be identified by its characteristic odour and by the blackening of filter paper moistened with lead acetate solution; alternatively, filter paper moistened with cadmium acetate solution is turned yellow ( $\text{CdS}$ ). A more sensitive test is attained by the use of sodium plumbite solution. prepared by adding sodium hydroxide solution to lead

\* Or dilute sulphuric acid.

acetate solution until the initial precipitate of lead hydroxide has just dissolved.



Hydrogen sulphide, like sulphur dioxide, is a good reducing agent; it reduces (1) acidified potassium permanganate solution, (ii) acidified potassium dichromate solution and (iii) iodine solution.



Small quantities of chlorine may be produced in (i) and (ii) if the hydrochloric acid is other than very dilute; this is avoided by using dilute sulphuric acid.

**2. Silver Nitrate Solution:** black precipitate of silver sulphide  $\text{Ag}_2\text{S}$ , insoluble in cold, but soluble in hot dilute nitric acid.

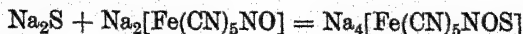


**3. Lead Acetate Solution:** black precipitate of lead sulphide  $\text{PbS}$  (see under Lead, Section III, 2, reaction 5).

**4. Barium Chloride Solution:** no precipitate.

**5. Silver.**—When a solution of a sulphide is brought into contact with a bright silver coin, a brown to black stain of silver sulphide is produced. The result is obtained more expeditiously by the addition of a few drops of dilute hydrochloric acid. The stain may be removed by rubbing the coin with moist lime.

**6. Sodium Nitroprusside Solution ( $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ ):** transient purple colour in the presence of solutions of alkalis. No reaction occurs with solutions of hydrogen sulphide or with the free gas: if, however, filter paper is moistened with a solution of the reagent made alkaline with sodium hydroxide or ammonia solution, a purple coloration is produced with free hydrogen sulphide.

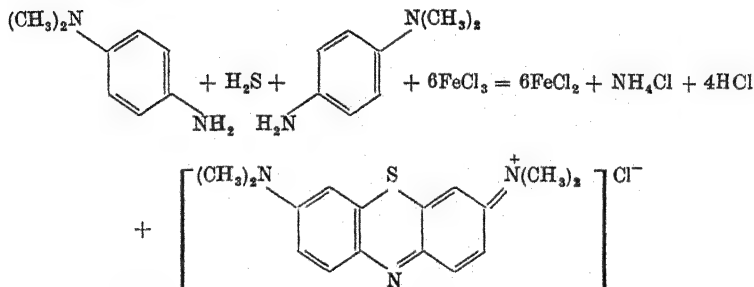


The reagent must be freshly prepared by dissolving a crystal (about the size of a pea) of pure sodium nitroprusside in a little distilled water.

† The spot-test technique is as follows. Mix on a spot plate a drop of the alkaline test solution with a drop of a 1 per cent solution of sodium nitroprusside. A violet colour appears. Alternatively, filter paper impregnated with an ammoniacal (5 per cent) solution of sodium nitroprusside may be employed.

Sensitivity: 1  $\mu\text{g. Na}_2\text{S}$ . Concentration limit: 1 in 50,000.

†7. **Methylene Blue Test.**—*para*-Aminodimethylaniline is converted by ferric chloride and hydrogen sulphide in strongly acid solution into the water-soluble dyestuff, methylene blue:



This is a sensitive test for soluble sulphides and hydrogen sulphide.

Place a drop of the test solution on a spot plate, add a drop of concentrated hydrochloric acid, mix, then dissolve a few grains of *p*-aminodimethylaniline in the mixture (or add 1 drop of a 1 per cent solution of the chloride or sulphate) and add a drop of 0.1N ferric chloride solution. A clear blue coloration appears after a short time (2–3 minutes).

Sensitivity: 1  $\mu\text{g. H}_2\text{S}$ . Concentration limit: 1 in 50,000.

†8. **Catalysis of Iodine-Azide Reaction Test.**—Solutions of sodium azide  $\text{NaN}_3$  and of iodine (as  $\text{KI}_3$ ) do not react, but on the addition of a trace of a sulphide, which acts as a catalyst, there is an immediate evolution of nitrogen:



Thiosulphates and thiocyanates act similarly and must therefore be absent. The sulphide can, however, be separated by precipitation with zinc or cadmium carbonate. The precipitated sulphide may then be introduced, say, at the end of a platinum wire into a semimicro test-tube or centrifuge tube containing the iodine-azide reagent, when the evolution of nitrogen will be seen.

Mix a drop of the test solution and a drop of the reagent on a watch glass. An immediate evolution of gas in the form of fine bubbles occurs.

Sensitivity: 0.3  $\mu\text{g. Na}_2\text{S}$ . Concentration limit: 1 in 166,000.

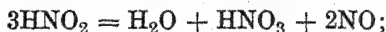
The sodium azide-iodine reagent is prepared by dissolving 3 grams of sodium azide in 100 ml. of 0.1N iodine. The solution is stable. {The test is rendered more sensitive (to 0.02  $\mu\text{g. Na}_2\text{S}$ ) by employing a more concentrated reagent composed of 1 gram of sodium azide and a few crystals of iodine in 3 ml. of water.}

IV, 7. REACTIONS OF NITRITES,  $\text{NO}_2^-$ 

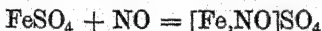
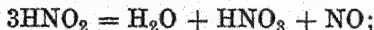
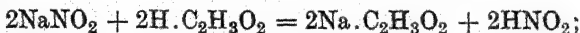
*Solubility.*—Silver nitrite is sparingly soluble in water. All other nitrites are soluble in water.

Use sodium nitrite,  $\text{NaNO}_2$ .

**1. Dilute Hydrochloric Acid.**—Cautious addition of the acid to a solid nitrite in the cold yields a transient, pale-blue liquid (due to the presence of free nitrous acid  $\text{HNO}_2$  or its anhydride  $\text{N}_2\text{O}_3$ ) and the evolution of brown fumes of nitrogen dioxide, the latter being largely produced by combination of nitric oxide with the oxygen of the air. Similar results are obtained with the aqueous solution.



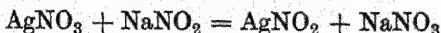
**2. Ferrous Sulphate Solution.**—When the nitrite solution is added carefully to a concentrated solution of ferrous sulphate acidified with dilute acetic acid or with dilute sulphuric acid, a brown ring, due to the compound  $[\text{Fe}, \text{NO}]\text{SO}_4$ , is formed at the junction of the two liquids. If the addition has not been made cautiously, a brown coloration results. This reaction is similar to the brown ring test for nitrates (see Section IV, 18, reaction 3), for which a stronger acid (concentrated sulphuric acid) must be employed.



Iodides, bromides, coloured ions and anions that give coloured compounds with ferrous salts must be absent.

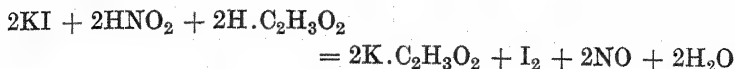
**3. Barium Chloride Solution:** no precipitate.

**4. Silver Nitrate Solution:** white crystalline precipitate of silver nitrite from concentrated solutions

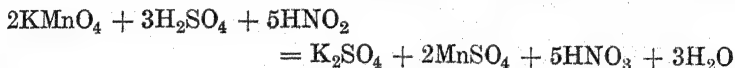


**5. Potassium Iodide Solution.**—The addition of a nitrite solution to a solution of potassium iodide, followed by acidification with acetic acid or with dilute sulphuric acid, results in the liberation of iodine, which may be identified by the blue colour produced with starch paste. A similar result is obtained

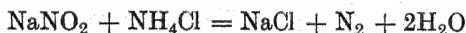
by dipping potassium iodide-starch paper moistened with a little dilute acid into the solution. An alternative method is to extract the liberated iodine with chloroform or carbon tetrachloride (see Section IV, 16, reaction 4).



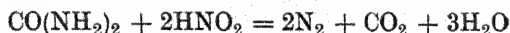
**6. Acidified Potassium Permanganate Solution:** decolourised by a solution of a nitrite, but no gas is evolved.



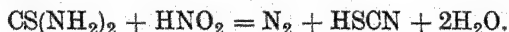
**7. Ammonium Chloride.**—By boiling a solution of a nitrite with excess of the solid reagent, nitrogen is evolved and the nitrite is completely destroyed.



**8. Urea**  $\{\text{CO}(\text{NH}_2)_2\}$ .—When a solution of a nitrite is treated with urea and the mixture acidified with dilute hydrochloric acid, the nitrite is decomposed, and nitrogen and carbon dioxide are evolved.

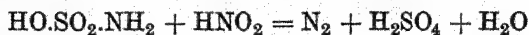


**9. Thiourea**  $\{\text{CS}(\text{NH}_2)_2\}$ .—When a dilute acetic acid solution of a nitrite is treated with a little thiourea, nitrogen is evolved and thiocyanic acid is produced. The latter may be identified by the red colour produced with dilute HCl and  $\text{FeCl}_3$  solution.



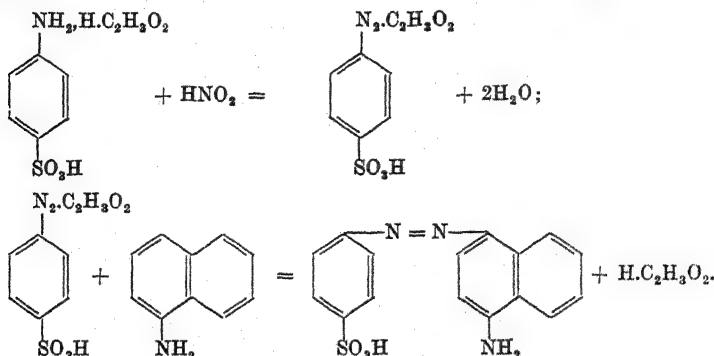
Thiocyanates and iodides interfere and, if present, must be removed either with excess of solid  $\text{Ag}_2\text{SO}_4$  or with dilute  $\text{AgNO}_3$  solution before adding the acetic acid and thiourea.

**10. Sulphamic Acid**  $(\text{HO} \cdot \text{SO}_2 \cdot \text{NH}_2)$ .—When a solution of a nitrite is treated with sulphamic acid, it is completely decomposed:



No nitrate is formed in this reaction, and it is therefore an excellent method for the complete removal of nitrite. Traces of nitrates are formed with ammonium chloride, urea and thiourea (reactions 7, 8 and 9).

†11. **Sulphanilic Acid- $\alpha$ -Naphthylamine Reagent.**—This test depends upon the diazotisation of sulphanilic acid by nitrous acid, followed by coupling with  $\alpha$ -naphthylamine to form a red azo dye:



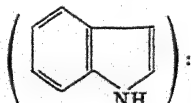
Ferric salts must be masked by tartaric acid.

Place a drop of the neutral or acetic acid test solution on a spot plate and mix it with a drop of the sulphanilic acid reagent, followed by a drop of the  $\alpha$ -naphthylamine reagent. A red colour is formed.

Sensitivity: 0.01  $\mu\text{g}$ .  $\text{HNO}_2$ . Concentration limit: 1 in 5,000,000.

The **sulphanilic acid reagent** is prepared by dissolving 1 gram of sulphanilic acid in 100 ml. of warm 30 per cent acetic acid. The  **$\alpha$ -naphthylamine reagent** is prepared by boiling 0.3 gram of  $\alpha$ -naphthylamine with 70 ml. of water, filtering or decanting from the small residue, and mixing with 30 ml. of glacial acetic acid.

#### †12. Indole Reagent



a red-coloured nitroso-indole is formed.

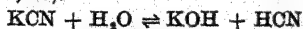
Place a drop of the test solution in a semimicro test-tube, add 10 drops of the reagent and 5 drops of 15*N* sulphuric acid. A purplish-red coloration appears.

Concentration limit: 1 in 1,000,000.

The **reagent** consists of a 0.015 per cent solution of indole in 96 per cent alcohol.

### IV, 8. REACTIONS OF CYANIDES, $\text{CN}^-$

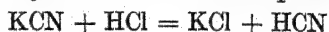
**Solubility.**—Only the cyanides of the alkali and alkaline earth metals are soluble in water; the solutions react alkaline owing to hydrolysis. Mercuric cyanide  $\text{Hg}(\text{CN})_2$  is also soluble in water, but is practically a non-electrolyte and therefore does not exhibit the ionic reactions of cyanides. Many of the metallic cyanides dissolve in solutions of potassium cyanide to yield complex salts (compare Section I, 20).



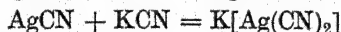
Use potassium cyanide, KCN.

*Note.* All cyanides are highly poisonous. The free acid HCN is volatile and is particularly dangerous so that all experiments in which the gas is likely to be evolved, or those in which cyanides are heated, should be carried out in the fume cupboard.

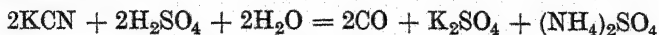
**1. Dilute Hydrochloric acid:** hydrocyanic acid HCN, with an odour reminiscent of bitter almonds, is evolved in the cold. It should be smelled with great caution. A more satisfactory method for identifying hydrocyanic acid consists in converting it into ammonium thiocyanate by allowing the vapour to come into contact with a little *yellow* ammonium sulphide on filter paper. The paper may be conveniently placed over the test-tube or dish in which the substance is being treated with the dilute acid. Upon adding a drop of ferric chloride solution and a drop of dilute hydrochloric acid to the filter paper, the characteristic red coloration, due to the ferri-thiocyanate ion  $[\text{Fe}(\text{SCN})]^{++}$ , is obtained (see reaction 6 below). Mercuric cyanide is not decomposed by dilute acids.



**2. Silver Nitrate Solution:** white precipitate of silver cyanide AgCN, readily soluble in excess of the cyanide solution forming the complex salt, potassium argentocyanide  $\text{K}[\text{Ag}(\text{CN})_2]$  (compare Section I, 20). Silver cyanide is soluble in ammonia solution and in sodium thiosulphate solution, but is insoluble in dilute nitric acid.

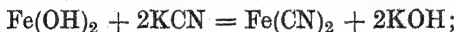
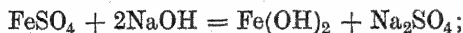


**3. Concentrated Sulphuric Acid.**—Heat a little of the solid salt with concentrated sulphuric acid; carbon monoxide is evolved which may be ignited and burns with a blue flame. All cyanides, complex and simple, are decomposed by this treatment.

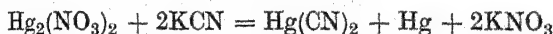


**4. Prussian Blue Test.**—This is a delicate test and is carried out in the following manner. The solution of the cyanide is rendered strongly alkaline with sodium hydroxide solution, a few ml. of a freshly prepared solution of ferrous sulphate added (if only traces of cyanide are present, it is best to use a saturated solution of ferrous sulphate) and the mixture boiled. Potassium ferrocyanide is thus formed. Upon acidifying with hydrochloric acid (in order to neutralise any free alkali which may be present), a clear solution is obtained,

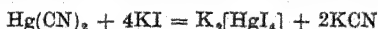
which gives a precipitate of Prussian blue upon the addition of a little ferric chloride solution. If only a little cyanide was used, or is present, in the solution to be tested, a green solution is obtained at first; this deposits Prussian blue on standing.



**5. Mercurous Nitrate Solution:** grey precipitate of metallic mercury (difference from chloride, bromide and iodide).



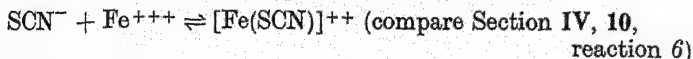
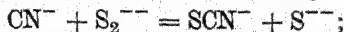
Mercuric cyanide is very little ionised in solution. It is best analysed by adding excess of potassium iodide solution when the cyanogen is obtained in an ionisable form:



Mercuric cyanide is decomposed in solution by hydrogen sulphide, mercuric sulphide (solubility product  $4 \times 10^{-53}$ ) being precipitated (compare Solubility Product, Section I, 15) and hydrocyanic acid being formed in solution. If the precipitate is filtered off, the thiocyanate test may be applied to the solution.



**6. "Ferri-thiocyanate" Test.**—This is another excellent test for cyanides and depends upon the direct combination of alkali cyanides with sulphur (best derived from an alkali polysulphide). A little ammonium polysulphide solution is added to the potassium cyanide solution contained in a porcelain dish, and the whole evaporated to dryness on the water bath in the fume cupboard. The residue contains alkali and ammonium thiocyanates together with any residual polysulphide. The latter is destroyed by the addition of a few drops of hydrochloric acid. One or two drops of ferric chloride solution are then added. A blood-red coloration, due to the complex ferri-thiocyanate cation, is produced immediately:



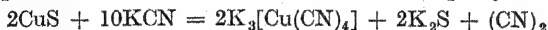
† The spot-test technique is as follows. Stir a drop of the test solution with a drop of yellow ammonium sulphide on a watch glass and warm until a rim of sulphur is formed round the liquid (evaporation to dryness, other than on a water bath, should be avoided). Add 1-2 drops of dilute hydrochloric acid, allow to cool, and add 1-2 drops of 3 per cent ferric chloride solution. A red coloration is obtained.

Sensitivity: 1  $\mu\text{g}$ .  $\text{CN}^-$ . Concentration limit: 1 in 50,000.



The test is applicable in the presence of sulphide or sulphite; if thiocyanate is originally present, the cyanide must be isolated first by precipitation, e.g. as zinc cyanide.

†7. **Copper Sulphide Test.**—Solutions of cyanides readily dissolve cupric sulphide forming the colourless potassium cuprocyanide:



The test is best carried out on filter paper or drop-reaction paper and is applicable in the presence of chlorides, bromides, iodides, ferro- and ferri-cyanides.

Place a drop of a freshly prepared copper sulphide suspension on a filter paper (or on a spot plate) and add a drop of the test solution. The brown colour of copper sulphide disappears at once.

Sensitivity: 2.5  $\mu\text{g}$ .  $\text{CN}^-$ . Concentration limit: 1 in 20,000.

The **copper sulphide suspension** is prepared by dissolving 0.12 gram of crystallised copper sulphate in 100 ml. of water, adding a few drops of ammonia solution and rendering the solution cloudy with a little hydrogen sulphide.

An *alternative procedure* is to employ quantitative filter paper or drop-reaction paper which has been impregnated with an ammoniacal solution containing 0.1 gram of copper sulphate per 100 ml. and dried. Immediately before the test a little hydrogen sulphide is blown on to the paper so that it acquires a uniform brown colour. Place a drop of the test solution upon this paper when a white ring will be obtained.

Sensitivity: 2.5  $\mu\text{g}$ .  $\text{CN}^-$ . Concentration limit: 1 in 20,000.

†8. **Copper Acetate-Benzidine Acetate Test.**—This reaction takes place because the oxidation potential of cupric copper is increased when cuprous copper is removed by cyanide ions.

Mix a few drops of the test solution with a little dilute sulphuric acid in a micro test-tube and tie (or otherwise fix) a piece of drop reaction paper which has been moistened with a mixture of equal parts of the copper acetate and benzidine reagents on to the top of the tube. A blue coloration is produced.

Sensitivity: 0.25  $\mu\text{g}$ .  $\text{CN}^-$ . Concentration limit: 1 in 200,000.

Oxidising and reducing gases interfere: it has been recommended that the hydrocyanic acid be liberated by heating with sodium bicarbonate.

Alternatively, place a drop of the test solution (or a few milligrams of the test solid) in the reaction bulb of Fig. II, 6, 13, add 2 thin pieces of zinc foil and 2-3 drops of dilute sulphuric acid. Place a small circle of quantitative filter paper (or drop reaction paper) moistened with cupric acetate-benzidine acetate reagent across the funnel. The paper is coloured blue by the hydrocyanic acid carried over with the hydrogen.

Sensitivity: 1  $\mu\text{g}$ .  $\text{CN}^-$ . Concentration limit: 1 in 50,000.

The **copper acetate reagent** (solution I) is a 3 per cent solution of copper acetate in water.

The **benzidine reagent** (solution II) is a 1 per cent solution of benzidine in 10 per cent acetic acid.

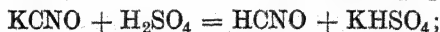
These solutions are best kept apart in black well-stoppered bottles. Equal volumes of solutions I and II are mixed immediately before required.

IV, 9. REACTIONS OF CYANATES, CNO<sup>-</sup>

*Solubility.*—The cyanates of the alkalis and of the alkaline earths are soluble in water. Those of silver, mercurous mercury, lead and copper are insoluble in water. The free acid is a colourless liquid with an unpleasant odour; it is very unstable.

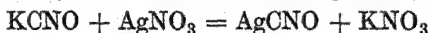
Use potassium cyanate, KCNO.

1. **Dilute Sulphuric Acid:** vigorous effervescence, due largely to the evolution of carbon dioxide. The free cyanic acid HCNO, which is liberated initially, is decomposed into carbon dioxide and ammonia, the latter combining with the sulphuric acid present to form ammonium sulphate. A little cyanic acid, however, escapes decomposition and may be recognised in the evolved gas by its penetrating odour. Upon warming the resulting solution with sodium hydroxide solution, ammonia is evolved (test with mercurous nitrate paper).



2. **Concentrated Sulphuric Acid.**—The reaction is similar to that with the dilute acid, but is somewhat more vigorous.

3. **Silver Nitrate Solution:** white, curdy precipitate of silver cyanate AgCNO, soluble in ammonia solution and in dilute nitric acid (difference from silver cyanide).



4. **Barium Chloride Solution:** no precipitate.

5. **Cobalt Acetate Solution.**—When the reagent is added to a concentrated solution of potassium cyanate, a blue coloration, due to potassium cobaltocyanate  $\text{K}_2[\text{Co}(\text{CNO})_4]$ , is produced. The colour is stabilised and intensified somewhat by the addition of ethyl alcohol.



6. **Copper Sulphate-Pyridine Test.**—When a cyanate is added to a dilute solution of a copper salt to which a few drops of pyridine have been previously added, a lilac blue precipitate is formed of the compound  $[\text{Cu}(\text{C}_5\text{H}_5\text{N})_2(\text{CNO})_2]$ ; this is soluble in chloroform with the production of a sapphire blue solution. Thiocyanates interfere; excess of copper solution should be avoided.

† Add a few drops of pyridine to 2–3 drops of a 1 per cent solution of copper sulphate in about 10 ml. of water, then introduce about 2 ml. of chloroform followed by a few drops of the neutral cyanate solution. Shake the mixture briskly: the chloroform will acquire a blue colour.

Concentration limit: 1 part cyanate in 20,000.

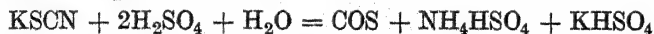
The blue complex is stable in the presence of a moderate excess of acetic acid; the reaction can therefore be applied to the detection of cyanates in alkaline solution. The solution to be tested is added to the copper-pyridine-chloroform mixture, acetic acid added slowly and the solution shaken vigorously after each addition. As soon as the solution is neutral, the chloroform will assume a blue colour.

#### IV, 10. REACTIONS OF THIOCYANATES, $\text{SCN}^-$ \*

*Solubility.*—Silver and cuprous thiocyanates are practically insoluble in water, mercuric and lead thiocyanates are sparingly soluble; the solubilities, in grams per litre at  $20^\circ$ , are 0.0003, 0.0005, 0.7 and 0.45 respectively. The thiocyanates of most other metals are soluble.

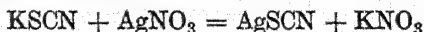
Use potassium thiocyanate (or sulphocyanide),  $\text{KSCN}$ .

**1. Sulphuric Acid.**—With the concentrated acid a yellow coloration is produced in the cold: upon warming a violent reaction occurs, carbonyl sulphide (burns with a blue flame) and sulphur dioxide (fuchsin solution decolourised) may be detected in the gaseous decomposition products, and a yellow residue of sulphur remains.



With the 5*N* acid no reaction occurs in the cold, but on boiling a yellow solution is formed, sulphur dioxide and a little carbonyl sulphide are evolved. A similar but slower reaction takes place with 2*N* sulphuric acid.

**2. Silver Nitrate Solution:** white, curdy precipitate of silver thiocyanate  $\text{AgSCN}$ , soluble in ammonia solution but insoluble in dilute nitric acid.



Upon boiling with *N* sodium chloride solution, silver thiocyanate is converted into silver chloride ( $\text{AgSCN} + \text{NaCl} \rightleftharpoons \text{AgCl} + \text{NaSCN}$ —distinction and method of separation from the silver halides); the aqueous solution may be acidified with dilute hydrochloric acid and ferric chloride solution added when the characteristic red coloration of the ferri-thiocyanate ion will be obtained.

Silver thiocyanate also decomposes upon ignition or upon fusion with sodium carbonate.

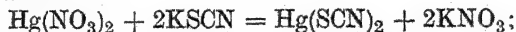
**3. Copper Sulphate Solution:** solution is coloured green; with excess of the reagent, black cupric thiocyanate  $\text{Cu}(\text{SCN})_2$

\* Raman spectra of thiocyanates appear to indicate that the ion is  $\text{S} - \text{C} \equiv \text{N}$  rather than  $\text{S} = \text{C} = \text{N}$ , since a line assignable to the triple link and none for the double link was observed. Salts will be written as, e.g.,  $\text{KSCN}$  and the ion  $[\text{SCN}]^-$  or  $\text{SCN}^-$ .

is precipitated. If a mixture of solutions of cupric sulphate and sulphurous acid is added to the thiocyanate solution, white cuprous thiocyanate  $\text{CuSCN}$  is precipitated; it is insoluble in dilute hydrochloric and sulphuric acids.



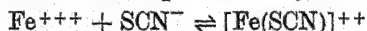
**4. Mercuric Nitrate Solution:** white precipitate of mercuric thiocyanate  $\text{Hg}(\text{SCN})_2$ , readily soluble in excess of the thiocyanate solution. If the precipitate is heated, it swells up enormously forming "Pharaoh's serpents," a polymerised cyanogen product.



**5. Zinc and Dilute Hydrochloric Acid:** hydrogen sulphide and hydrogen cyanide (*poisonous*) are evolved.



**6. Ferric Chloride Solution:** blood red coloration, due to the complex ferri-thiocyanate cation  $[\text{Fe}(\text{SCN})]^{++}$ .\* The colour can be extracted by shaking with ether. The red colour is discharged by fluorides ( $[\text{FeF}_6]^{---}$  formed), mercuric chloride ( $[\text{Hg}(\text{SCN})_4]^{--}$  formed) and oxalates ( $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{---}$  formed). Tartrates, other hydroxy acids, ferrocyanides, phosphates, sulphides, thiosulphates and iodides interfere (the last-named because free iodine is produced by the ferric ions).



**7. Dilute Nitric Acid:** decomposition occurs upon warming, a red coloration is produced, and nitric oxide and hydrogen cyanide (*poisonous*) are evolved.



A vigorous reaction occurs with concentrated nitric acid, nitric oxide and carbon dioxide being evolved.

†**8. Thiocyanic Acid ( $\text{HSCN}$ ) Distillation Test.**—This test is a modification of 6, and avoids interferences such as those due to iodides and ferrocyanides.

Place a few drops of the test solution in a semimicro test-tube, acidify with dilute hydrochloric acid, add a small fragment of broken porcelain and attach a gas absorption pipette (Fig. II, 3, 19, c) charged with a drop or two of ammonia solution. Boil the solution in the test-tube gently so as to distil any  $\text{HSCN}$  present into the ammonia solution. Rinse the ammonia solution into a clean semimicro test-tube, acidify

\* At high concentrations of thiocyanate there is some evidence that  $[\text{Fe}(\text{SCN})_6]^{+}$  also exists in solution: the complexes have been formulated as  $[\text{Fe}(\text{SCN})_6]^{(3-2)}$ . The evidence for the presence of  $[\text{Fe}(\text{SCN})]^{++}$  seems indisputable and this formula will be adopted throughout this book.

slightly with dilute hydrochloric acid and add a drop of ferric chloride solution. A red coloration is obtained.

**9. Cobalt Nitrate Solution:** blue coloration, due to  $K_2[Co(CNS)_4]$  (see under Cobalt, Section III, 24, reaction 6), but no precipitate (distinction from cyanide, ferrocyanide and ferricyanide).

† The spot-test technique is as follows. Mix a drop of the test solution in a micro-crucible with a very small drop (0.02 ml.) of a 1 per cent solution of cobalt sulphate or nitrate and evaporate to dryness. The residue, whether thiocyanate is present or not, is coloured violet and the colour slowly fades. Add a few drops of acetone. A blue-green or green coloration is obtained.

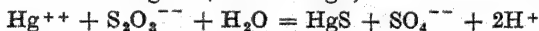
Sensitivity: 1  $\mu$ g.  $SCN^-$ . Concentration limit: 1 in 50,000.

Nitrites yield a red colour due to nitrosyl thiocyanate and therefore interfere with the test.

† **10. Catalysis of Iodine-Azide Reaction Test.**—Traces of thiocyanates act as powerful catalysts in the otherwise extremely slow reaction between iodine and sodium azide:



Sulphides (see Section IV, 6, reaction 8) and thiosulphates (see Section IV, 5, reaction 9) have a similar catalytic effect; these may be removed by precipitation with mercuric chloride solution:



Considerable amounts of iodine retard the reaction; iodine is therefore best largely removed by the addition of cold saturated mercuric chloride solution whereupon the complex  $[HgI_4]^{--}$  ion, which does not affect the catalysis, is formed.

Mix a drop of the test solution with 1 drop of the iodine-azide reagent on a spot plate. Bubbles of gas (nitrogen) are evolved.

Sensitivity: 1.5  $\mu$ g. KSCN. Concentration limit: 1 in 30,000.

The reagent is prepared by dissolving 3 grams of sodium azide in 100 ml. of 0.1N iodine.

**11. Cupric Sulphate-Pyridine Reagent.**—When a neutral solution of a thiocyanate is added to a dilute solution of a copper salt containing a few drops of pyridine, a yellowish-green precipitate of the composition  $[Cu(C_5H_5N)_2(SCN)_2]$  is formed; the compound is soluble in chloroform to which it imparts an emerald green coloration. Cyanates interfere with this reaction; excess of pyridine should be avoided.

† Add a few drops of pyridine to 3–4 drops of a 1 per cent solution of copper sulphate in about 5 ml. of water, then introduce about 2 ml. of chloroform, followed by a few drops of the neutral thiocyanate solution. Shake the mixture vigorously. The chloroform will acquire a green colour.

Concentration limit: 1 part thiocyanate in 50,000.

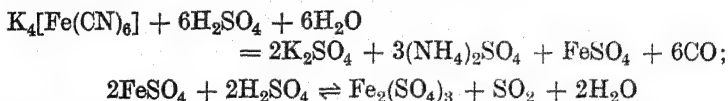
## IV, 11. REACTIONS OF FERROCYANIDES,



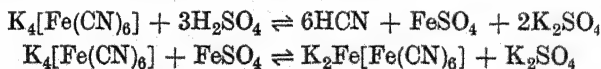
*Solubility.*—The ferrocyanides of the alkali and alkaline earth metals are soluble in water; those of the other metals are insoluble in water and in cold dilute acids, but are decomposed by alkalis.

Use potassium ferrocyanide,  $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ .

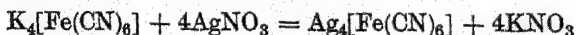
**1. Concentrated Sulphuric Acid:** complete decomposition occurs on prolonged boiling with the evolution of carbon monoxide, which burns with a blue flame. A little sulphur dioxide may also be produced, due to the reduction of the sulphuric acid by some of the ferrous sulphate.



With dilute sulphuric acid, little reaction occurs in the cold, but on boiling a partial decomposition of the ferrocyanide occurs with the evolution of hydrogen cyanide and the formation of some ferrous sulphate. The latter reacts with some of the undecomposed ferrocyanide yielding initially a precipitate of  $\text{K}_2\text{Fe}[\text{Fe}(\text{CN})_6]$ , which is gradually oxidised to Prussian blue (see under Iron, Section III, 19, reaction 6).



**2. Silver Nitrate Solution:** white precipitate of silver ferrocyanide  $\text{Ag}_4[\text{Fe}(\text{CN})_6]$ , insoluble in ammonia solution (distinction from ferricyanide) and in dilute nitric acid, but soluble in potassium cyanide solution and in sodium thiosulphate solution. Upon warming with concentrated nitric acid, the precipitate is converted into the orange-red silver ferricyanide and is then soluble in ammonia solution.



**3. Ferric Chloride Solution:** precipitate of Prussian blue  $\text{KFe}[\text{Fe}(\text{CN})_6]$  in neutral and acid solutions (see under Iron, Section III, 20, reaction 5); the precipitate is decomposed by solutions of caustic alkalis, brown ferric hydroxide being formed.

† The spot-test technique is as follows. Mix a drop of the test solution on a spot plate with a drop of ferric chloride solution. A blue precipitate or stain is formed.

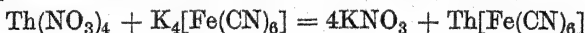
Sensitivity:  $1.3 \mu\text{g}$ .  $\text{K}_4[\text{Fe}(\text{CN})_6]$ . Concentration limit: 1 in 400,000.

**4. Ferrous Sulphate Solution:** white precipitate of potassium ferrous ferrocyanide  $K_2Fe[Fe(CN)_6]$ , rapidly turning blue owing to oxidation (see under Iron, Section II, 19, reaction 6).

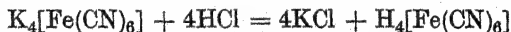
**5. Copper Sulphate Solution:** brown precipitate of copper ferrocyanide  $Cu_2[Fe(CN)_6]$ , insoluble in dilute acetic acid, but decomposed by solutions of caustic alkalis.



**6. Thorium Nitrate Solution:** white precipitate of thorium ferrocyanide  $Th[Fe(CN)_6]$ , which is difficult to filter (distinction and separation from ferricyanide and thiocyanate).



**7. Hydrochloric Acid.**—Treatment of a concentrated solution of potassium ferrocyanide with hydrochloric acid results in the formation of hydroferrocyanic acid  $H_4[Fe(CN)_6]$ , which may be isolated by extraction with ether, and obtained as a white solid.



**8. Ammonium Molybdate in Dilute Hydrochloric Acid Solution:** brown precipitate of molybdenyl ferrocyanide (distinction and separation from ferricyanide and thiocyanate), insoluble in dilute acids but soluble in solutions of alkali hydroxides.

**9. Titanium Chloride Reagent Test.**—Ferrocyanides give with the pale yellow solution of titanium tetrachloride in dilute hydrochloric acid a reddish-brown, flocculent precipitate of titanium ferrocyanide  $Ti[Fe(CN)_6]$ , which is insoluble in 6*N* hydrochloric acid. Ferricyanides give no precipitate: anions (*e.g.* chromate, arsenate and nitrite) which oxidise ferrocyanides interfere.

† Place a drop of the test solution on a spot plate, just acidify with dilute hydrochloric acid, and introduce 1 drop of the reagent. A reddish-brown precipitate is produced by ferrocyanides.

The reagent is prepared (FUME CUPBOARD) by adding 10 ml. of liquid  $TiCl_4$  to 90 ml. of dilute hydrochloric acid (1 : 1).

**10. Cobalt Nitrate Solution:** greyish-green precipitate of cobalt ferrocyanide  $Co_2[Fe(CN)_6]$  with excess of the reagent, insoluble in dilute hydrochloric and dilute acetic acids.

†11. **Uranyl Acetate Solution:** brown precipitate of uranyl ferrocyanide  $(UO_2)_2[Fe(CN)_6]$  in the presence of dilute acetic acid. Ferricyanides react only in concentrated solutions, and after long standing or heating to give the dirty yellow uranyl ferricyanide. Ferricyanides

are reduced by filter paper to ferrocyanides, hence the test should not be carried out on filter paper.

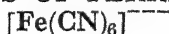
Place a drop of the test solution on a spot plate and add a drop of *N* uranyl acetate solution. A brown precipitate or spot is obtained within 2 minutes.

Sensitivity: 1  $\mu$ g.  $K_4[Fe(CN)_6]$ . Concentration limit: 1 in 50,000.

**12. Action of Heat.**—All ferrocyanides are decomposed on heating, nitrogen and cyanogen being evolved.



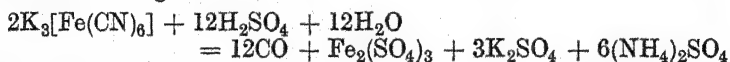
#### IV, 12. REACTIONS OF FERRICYANIDES,



*Solubility.*—The ferricyanides of the alkali and alkaline earth metals and of ferric iron are soluble in water; those of most of the other metals are insoluble or sparingly soluble.

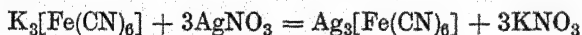
Use potassium ferricyanide,  $K_3[Fe(CN)_6]$ .

**1. Concentrated Sulphuric Acid.**—On warming a solid ferricyanide with this acid, it is decomposed completely, carbon monoxide being evolved.



With dilute sulphuric acid, no reaction occurs in the cold but on boiling hydrocyanic acid is evolved.

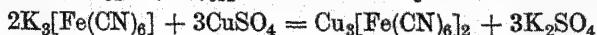
**2. Silver Nitrate Solution:** orange-red precipitate of silver ferricyanide  $Ag_3[Fe(CN)_6]$ , soluble in dilute ammonia solution (distinction from ferrocyanide), but insoluble in dilute nitric acid.



**3. Ferrous Sulphate Solution:** dark blue precipitate, formerly termed Turnbull's blue, but now known to be identical with Prussian blue  $KFe[Fe(CN)_6]$ , in neutral or acid solution (see under Iron, Section III, 19, reaction 7).

**4. Ferric Chloride Solution:** brown coloration, due to ferric ferricyanide  $Fe[Fe(CN)_6]$  (see under Iron, Section III, 20, reaction 6).

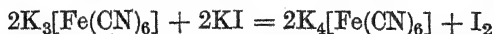
**5. Copper Sulphate Solution:** green precipitate of cupric ferricyanide  $Cu_3[Fe(CN)_6]_2$ , insoluble in hydrochloric acid.



**6. Concentrated Hydrochloric Acid.**—The addition of concentrated hydrochloric acid to a cold saturated solution of potassium ferricyanide results in the separation of brown ferri-cyanic acid  $H_3[Fe(CN)_6]$ .



7. **Potassium Iodide Solution:** iodine is liberated, which may be identified by the blue colour produced with starch solution.



8. **Cobalt Nitrate Solution:** red precipitate of cobalt ferri-cyanide  $Co_3[Fe(CN)_6]_2$ , insoluble in hydrochloric acid but soluble in ammonia solution.

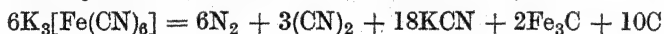
†9. **Benzidine Reagent:** blue precipitate of oxidation product. Other oxidising agents (molybdates, chromates, etc.) must be absent. The test is applicable in the presence of ferrocyanide for benzidine ferrocyanide is white; the sensitivity is, however, reduced and it is best to precipitate the ferrocyanide first as the white insoluble lead ferrocyanide by the addition of lead acetate, the ferricyanide remaining in solution.

Mix a drop of the test solution on a spot plate with a drop of the benzidine reagent. If ferrocyanides are present, a drop of 1 per cent lead nitrate solution should be added before the reagent. A blue precipitate or coloration appears.

Sensitivity: 1  $\mu$ g.  $K_3[Fe(CN)_6]$ . Concentration limit: 1 in 50,000.

The reagent consists of 2N acetic acid saturated with benzidine in the cold.

10. **Action of Heat.**—The decomposition is similar to that of ferrocyanides (Section IV, 11, reaction 12).



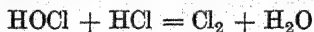
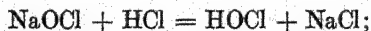
#### IV, 13. REACTION OF HYPOCHLORITES, $ClO^-$

*Solubility.*—All hypochlorites are soluble in water. The solutions are alkaline because of hydrolysis, and are decomposed by boiling.

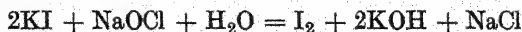


Use a solution of sodium hypochlorite,  $NaOCl$ .\*

1. **Dilute Hydrochloric Acid:** the solution at first assumes a yellow colour, effervescence occurs and chlorine is evolved. The gas may be identified (a) by its greenish-yellow colour and irritating odour, (b) by its bleaching of litmus paper and (c) by its action upon potassium iodide-starch paper which it turns blue-black.

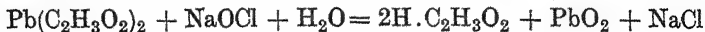


2. **Potassium Iodide-Starch Paper:** assumes a bluish-black colour in weakly alkaline solution as a result of the separation of iodine.



\* Chloride is invariably present, and this will vitiate many ionic reactions.

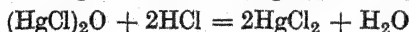
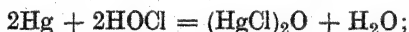
3. **Lead Acetate or Lead Nitrate Solution:** brown lead dioxide  $\text{PbO}_2$  is produced on boiling.



4. **Cobalt Nitrate Solution.**—Add a few drops of the reagent to a solution of the hypochlorite; a black precipitate of cobalt oxide is obtained. On warming, oxygen is evolved (identified by the rekindling of a glowing splint), the cobalt oxide acting as a catalyst.

5. **Mercury.**—On shaking a slightly acidified (sulphuric acid) solution of a hypochlorite with mercury, a brown precipitate of basic mercuric chloride  $(\text{HgCl})_2\text{O}$  is formed, which is insoluble in water, but soluble in dilute hydrochloric acid. The precipitate is filtered off and dissolved in dilute hydrochloric acid; a black precipitate of mercuric sulphide is obtained on passing hydrogen sulphide into the solution.

Chlorine water, under similar conditions, gives a white precipitate of mercurous chloride  $\text{Hg}_2\text{Cl}_2$ , insoluble in hydrochloric acid.



#### IV, 14. REACTIONS OF CHLORIDES, $\text{Cl}^-$

*Solubility.*—Most chlorides are soluble in water. Mercurous chloride  $\text{Hg}_2\text{Cl}_2$ , silver chloride  $\text{AgCl}$ , lead chloride  $\text{PbCl}_2$  (this is sparingly soluble in cold but readily soluble in boiling water), cuprous chloride  $\text{CuCl}$ , bismuth oxychloride  $\text{BiOCl}$ , antimony oxychloride  $\text{SbOCl}$  and mercuric oxychloride  $\text{Hg}_2\text{OCl}_2$  are insoluble in water.

Use sodium chloride,  $\text{NaCl}$ .

1. **Concentrated Sulphuric Acid:** considerable decomposition of the chloride occurs in the cold, completely on warming, with the evolution of hydrogen chloride, which is recognised (a) by its pungent odour and the production of white fumes, consisting of fine drops of hydrochloric acid, on blowing across the mouth of the tube, (b) by the formation of white clouds of ammonium chloride when a glass rod moistened with ammonia solution is held near the mouth of the vessel and (c) by its turning blue litmus paper red.



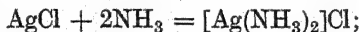
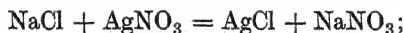
2. **Manganese Dioxide and Concentrated Sulphuric Acid.**—If the solid chloride is mixed with an equal quantity of precipitated manganese dioxide,\* concentrated sulphuric acid

\* The commercial substance (pyrolusite) usually contains considerable quantities of chlorides.

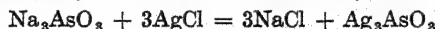
added and the mixture gently warmed, chlorine is evolved which is identified by its suffocating odour, yellowish-green colour, its bleaching of moistened litmus paper, and turning of potassium iodide-starch paper blue. The hydrogen chloride first formed is oxidised to chlorine.



**3. Silver Nitrate Solution:** white, curdy precipitate of silver chloride  $\text{AgCl}$ , insoluble in water and in dilute nitric acid, but soluble in *dilute ammonia* solution and in potassium cyanide and sodium thiosulphate solutions (see under Silver, Section III, 4, reaction 1; also Complex Ions, Section I, 20). The silver chloride is re-precipitated from the ammoniacal solution by the addition of dilute nitric acid.



If the silver chloride precipitate is filtered off, washed with distilled water and then shaken with sodium arsenite solution it is converted into yellow silver arsenite and sodium chloride is formed (distinction from silver bromide and silver iodide, which are unaffected by this treatment). This may be used as a confirmatory test for a chloride.



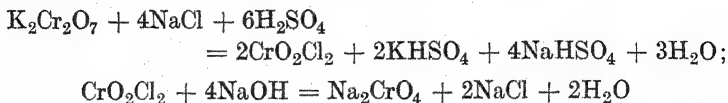
**4. Lead Acetate Solution:** white precipitate of lead chloride  $\text{PbCl}_2$  from concentrated solutions (see under Lead, Section III, 2, reaction 1).

**5. Potassium Dichromate and Sulphuric Acid (Chromyl Chloride Test).—**The solid chloride is intimately mixed with three times its weight of powdered potassium dichromate in a small distilling flask (Fig. IV, 2, 1), an equal bulk of concentrated sulphuric acid added and the mixture gently warmed.\* The deep-red vapours of chromyl chloride  $\text{CrO}_2\text{Cl}_2$  which are evolved are passed into sodium hydroxide solution contained in a test-tube. The resulting yellow solution in the test-tube contains sodium chromate; this is confirmed by acidifying with dilute sulphuric acid, adding 1–2 ml. of amyl alcohol† followed by a little hydrogen peroxide solution. The organic layer is coloured blue. Alternatively, the diphenylcarbazide reagent

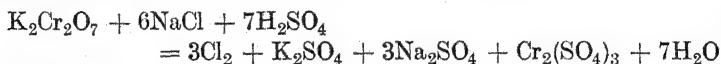
\* This test must not be carried out in the presence of chlorates because of the danger of forming explosive chlorine dioxide (Section IV, 19, reaction 1).

† Diethyl ether may also be used, but owing to its highly inflammable character and the possible presence of peroxides (unless previously removed by special treatment), it is preferable to employ amyl alcohol or, less efficiently, amyl acetate.

test (Section IV, 33, reaction 10) may be applied. The formation of a chromate in the distillate indicates that a chloride was present in the solid substance, since chromyl chloride is a readily volatile liquid (b.p.  $116.5^{\circ}\text{C}$ ).



Some chlorine may be liberated by the reaction:



and this decreases the sensitivity of the test.

Bromides and iodides give rise to the free halogens, which yield colourless solutions with sodium hydroxide: if the ratio of iodide to chloride exceeds 1 : 15, the chromyl chloride formation is largely prevented and chlorine is evolved.\* Fluorides give rise to the volatile chromyl fluoride  $\text{CrO}_2\text{F}_2$ , which is decomposed by water, and hence should be absent or removed. Nitrites and nitrates interfere as nitrosyl chloride may be formed. Chlorates must, of course, be absent.

The chlorides of mercury, owing to their slight ionisation, do not respond to this test. Only partial conversion to  $\text{CrO}_2\text{Cl}_2$  occurs with the chlorides of lead, silver, antimony and tin.

† The spot-test technique is as follows. Into the tube of Fig. II, 6, 14 place a few milligrams of the solid sample (or evaporate a drop or two of the test solution in it), add a small quantity of powdered potassium dichromate and a drop of concentrated sulphuric acid. Place a column about 1 mm. long of a 1 per cent solution of diphenylcarbazide in alcohol into the capillary of the stopper and heat the apparatus for a few minutes. The chromyl chloride evolved causes the reagent to assume a violet colour.

Sensitivity:  $1.5 \mu\text{g. Cl}^-$ . Concentration limit: 1 in 30,000.

Alternatively, employ the same quantities of materials in the apparatus of Fig. II, 6, 10, and replace the diphenylcarbazide solution by a drop of dilute alkali on the glass knob. Warm for a few minutes and, after cooling, dip the glass knob into a few drops of the alcoholic diphenylcarbazide solution which has been treated with a little dilute sulphuric acid and is contained on a spot plate. A violet coloration is obtained.

Sensitivity:  $0.3 \mu\text{g. Cl}^-$ . Concentration limit: 1 in 150,000.

\* The iodine reacts with the chromic acid yielding iodic acid: the latter, in the presence of concentrated sulphuric acid and especially on warming, liberates chlorine from chlorides, regenerating iodide. This explains the failure to form chromyl chloride.

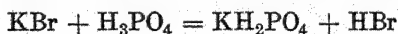
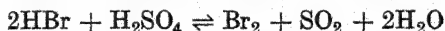
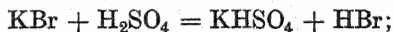
Small amounts of bromides (< 5 per cent) do not interfere, but large amounts of bromides give rise to sufficient bromine to oxidise the reagent. It is therefore best to add a little phenol to the reagent solution, whereupon the bromine is removed as tribromophenol. Nitrates interfere since nitrosyl chloride is formed, but they may be reduced to ammonium salts. The interference of iodides is discussed above.

#### IV, 15. REACTIONS OF BROMIDES, Br<sup>-</sup>

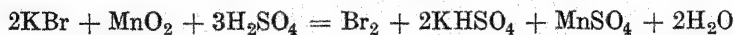
*Solubility.*—Silver, mercurous and cuprous bromides are insoluble in water. Lead bromide is sparingly soluble in cold, but more soluble in boiling water. All other bromides are soluble.

Use potassium bromide, KBr.

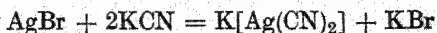
**1. Concentrated Sulphuric Acid.**—With the solid bromide, a reddish-brown solution is first formed and reddish-brown vapours of bromine accompany the hydrogen bromide (fuming in moist air) which is evolved; the reaction is accelerated by warming. The bromine is produced by the oxidation of the hydrogen bromide by the sulphuric acid. If syrupy phosphoric acid H<sub>3</sub>PO<sub>4</sub> is substituted for the sulphuric acid and the mixture warmed, only hydrogen bromide, the properties of which are similar to hydrogen chloride, is evolved.



**2. Manganese Dioxide and Concentrated Sulphuric Acid.**—When a mixture of a solid bromide, precipitated manganese dioxide and concentrated sulphuric acid is warmed, reddish-brown vapours of bromine are evolved, which is recognised (a) by its powerful irritating odour, (b) by its bleaching of litmus paper, (c) by its staining of starch paper orange-red and (d) by the red coloration produced upon filter paper impregnated with fluorescein (see Test 8 below).



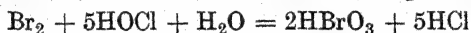
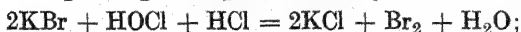
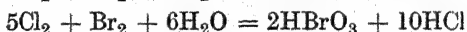
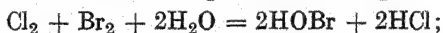
**3. Silver Nitrate Solution:** curdy, pale yellow precipitate of silver bromide AgBr, sparingly soluble in dilute, but readily soluble in concentrated ammonia solution. The precipitate is also soluble in potassium cyanide and sodium thiosulphate solutions, but insoluble in dilute nitric acid.



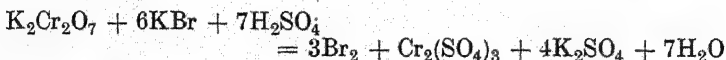
**4. Lead Acetate Solution:** white crystalline precipitate of lead bromide  $\text{PbBr}_2$ , sparingly soluble in cold, but soluble in boiling water.



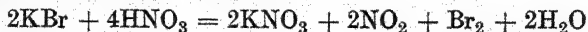
**5. Chlorine Water.\***—The addition of this reagent dropwise to a solution of a bromide liberates free bromine, which colours the solution orange-red; if carbon disulphide, chloroform or carbon tetrachloride (2 ml.) is added and the liquid shaken, the bromine dissolves in the solvent (see The Distribution Law, Section I, 43) and, after allowing to stand, forms a reddish-brown solution below the colourless aqueous layer. With excess of chlorine water, the bromine is converted into yellow bromine monochloride or into colourless hypobromous or bromic acid, and a pale-yellow or colourless solution results (difference from iodide).



**6. Potassium Dichromate and Concentrated Sulphuric Acid.**—On gently warming a mixture of a solid bromide, concentrated sulphuric acid and potassium dichromate (see Chlorides, Section IV, 14, reaction 5) and passing the evolved vapours into water, a yellowish-brown solution, containing free bromine but no chromium, is produced. A colourless (or sometimes a pale yellow) solution is obtained on treatment with sodium hydroxide solution; this does not give the chromate reaction with dilute sulphuric acid, hydrogen peroxide and amyl alcohol, or with the diphenylcarbazide reagent (distinction from chloride).



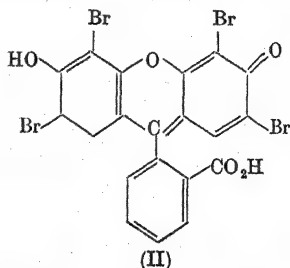
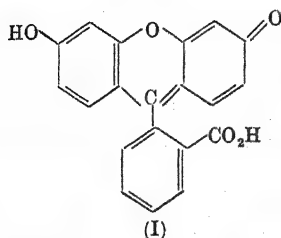
**7. Nitric Acid.**—Hot and fairly concentrated nitric acid oxidises bromides to bromine:



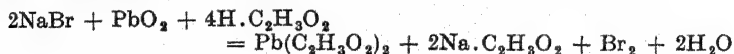
†**8. Fluorescein Test.**—Free bromine converts the yellow dyestuff fluorescein (I) into the red tetrabromo-fluorescein or eosin (II). Filter

\* In practice, it is more convenient to use dilute sodium hypochlorite solution, acidified with dilute hydrochloric acid. This may also react as hypochlorous acid,  $\text{HOCl}$ .

paper impregnated with fluorescein solution is therefore a valuable reagent for bromine vapour since the paper acquires a red colour.



Chlorine tends to bleach the reagent. Iodine forms the red-violet coloured iodo-eosin and hence must be absent. If the bromide is oxidised to free bromine by heating with lead dioxide and acetic acid, practically no chlorine is simultaneously evolved from chlorides, and hence the test may be conducted in the presence of chlorides.



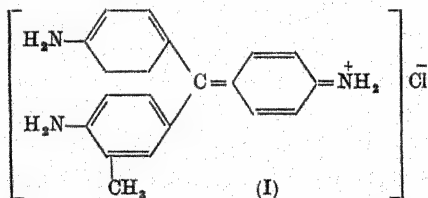
Place a drop of the test solution together with a few milligrams of lead dioxide and acetic acid into the apparatus of Fig. II, 6, 13, and close the tube with the funnel stopper carrying a piece of filter paper which has been impregnated with the reagent and dried. Warm the apparatus gently. A circular red spot is formed on the yellow test paper.

Alternatively, the apparatus of Fig. II, 6, 14 may be used; a column, about 1 mm. long of the reagent, is employed.

Sensitivity: 2  $\mu\text{g}$ .  $\text{Br}_2$ . Concentration limit: 1 in 25,000.

The **fluorescein reagent** consists of a saturated solution of fluorescein in 50 per cent alcohol.

† 2. **Fuchsin (or Magenta) Test.**—The dyestuff fuchsin (I) forms a



colourless addition compound with a bisulphite. Free bromine converts the thus decolourised fuchsin into a blue or violet brominated dyestuff. Neither free chlorine nor free iodine affect the colourless fuchsin bisulphite compound, hence the reaction may be employed for the detection of bromides in the presence of chlorides and iodides.

Place a drop of the test solution (or a few milligrams of the test solid) in the tube of the apparatus shown in Fig. II, 6, 14, add 2-4 drops of 25 per cent chromic acid solution and close the apparatus with the "head" which contains 1-2 drops of the reagent solution in the capillary.

Warm the apparatus gently (do not allow it to boil). In a short time the liquid in the capillary assumes a violet colour.

Sensitivity: 3  $\mu\text{g}$ .  $\text{Br}^-$ . Concentration limit: 1 in 15,000.

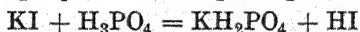
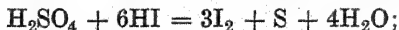
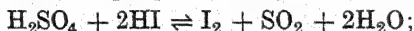
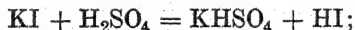
The **fuchsin-bisulphite reagent** consists of a 0.1 per cent fuchsin solution just decolourised by sodium bisulphite.

#### IV, 16. REACTION OF IODIDES, $\text{I}^-$

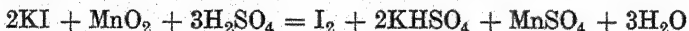
*Solubility.*—The solubilities of the iodides are similar to those of the chlorides and bromides. Silver, mercurous, mercuric, cuprous and lead iodides are the least soluble salts.

Use potassium iodide, KI.

**1. Concentrated Sulphuric Acid.**—With a solid iodide, iodine is liberated; on warming, violet vapours are evolved, which turn starch paper blue. Some hydrogen iodide is formed—this can be seen by blowing across the mouth of the vessel, when white fumes are produced—but most of it reduces the sulphuric acid to sulphur dioxide, hydrogen sulphide and sulphur, the relative proportions of which depend upon the concentrations of the reagents. Pure hydrogen iodide is formed on warming with syrupy phosphoric acid.



If manganese dioxide is added to the mixture, only iodine is evolved.



**2. Silver Nitrate Solution:** yellow, curdy precipitate of silver iodide  $\text{AgI}$ , readily soluble in potassium cyanide and in sodium thiosulphate solutions, very slightly soluble in concentrated ammonia solution, and insoluble in dilute nitric acid.



**3. Lead Acetate Solution:** yellow precipitate of lead iodide  $\text{PbI}_2$ , soluble in much hot water forming a colourless solution, and yielding golden-yellow plates ("spangles") on cooling.

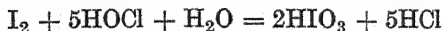
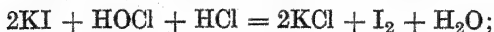
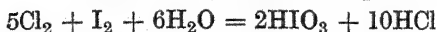


**4. Chlorine Water.\***—When this reagent is added dropwise to a solution of an iodide, iodine is liberated, which colours

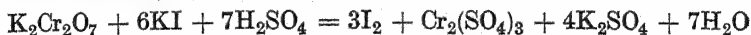
\* In practice it is more convenient to use dilute sodium hypochlorite solution acidified with dilute hydrochloric acid. This may react as hypochlorous acid,  $\text{HOCl}$ .



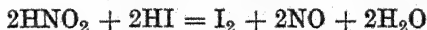
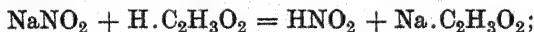
the solution brown; on shaking with 1-2 ml. of carbon disulphide, chloroform or carbon tetrachloride (see Section I, 43), it dissolves forming a violet solution, which settles out below the aqueous layer. The free iodine may also be identified by the characteristic blue colour it forms with starch solution. If excess of chlorine water is added, the iodine is oxidised to colourless iodic acid.



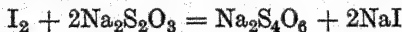
**5. Potassium Dichromate and Concentrated Sulphuric Acid:** only iodine is liberated, and no chromate is present in the distillate (see Chlorides, Section IV, 14, reaction 5) (difference from chloride).



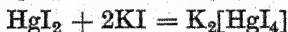
**6. Sodium Nitrite Solution.**—Iodine is liberated when this reagent is added to an iodide solution acidified with dilute acetic or sulphuric acid (difference from bromide and chloride). The iodine may be identified by colouring starch paste blue, or carbon tetrachloride violet.



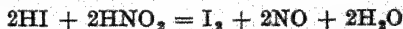
**7. Copper Sulphate Solution:** brown precipitate consisting of a mixture of cuprous iodide  $\text{CuI}$  and iodine. The iodine may be removed by the addition of sodium thiosulphate solution or sulphurous acid, and a nearly white precipitate of cuprous iodide obtained.



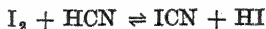
**8. Mercuric Chloride Solution:** scarlet precipitate of mercuric iodide  $\text{HgI}_2$ , soluble in excess of potassium iodide solution.



**†9. Starch Test.**—Iodides are readily oxidised in acid solution to free iodine by a number of oxidising agents; the free iodine may then be identified by the deep blue coloration produced with starch solution. The best oxidising agent to employ in the spot test reaction is acidified potassium nitrite solution:



Cyanides interfere because of the formation of cyanogen iodide; they are therefore removed before the test either by heating with sodium bicarbonate solution or by acidifying and heating:

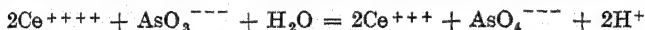


Mix a drop of the acid test solution on a spot plate with a drop of the reagent and add a drop of 10 per cent potassium nitrite solution. A blue coloration is obtained.

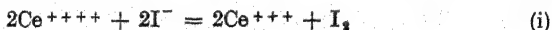
Sensitivity: 2.5  $\mu\text{g}$ .  $\text{I}_2$ . Concentration limit: 1 in 20,000.

The starch reagent is prepared by mixing 1 gram of soluble starch and 0.005 gram of mercuric iodide (which acts as a preservative) with a little water into a paste and then pouring 500 ml. of boiling water over the paste.

†10. **Catalytic Reduction of Ceric Salts Test.**—The reduction of ceric salts in acid solution by arsenites takes place very slowly:



Iodides accelerate this change, possibly owing to iodine liberated in the instantaneous reaction (i):



reacting according to (ii):



the iodide ion reacting again as in (i). The completion of the reduction is indicated by the disappearance of the yellow colour of the ceric solution. Osmium and ruthenium salts have a similar catalytic effect. Moderate amounts of chlorides, bromides, sulphates and nitrates have no influence, but cyanides and also mercuric, silver and manganese salts interfere.

Place a drop of the test solution together with a drop each of neutral or slightly acid 0.1N sodium arsenite solution and 0.05N ceric ammonium sulphate solution (in 2N sulphuric acid) on a spot plate. The yellow colour soon disappears.

Sensitivity: 0.03  $\mu\text{g}$ .  $\text{I}^-$ . Concentration limit: 1 in 1,000,000.

†11. **Palladous Chloride Test.**—Solutions of iodides react with palladous chloride solution to yield a brownish-red precipitate of palladous iodide  $\text{PdI}_2$ , insoluble in mineral acids.

Mix a drop of the test solution on drop-reaction paper with a drop of a 1 per cent aqueous solution of palladous chloride. A brownish-black precipitate forms.

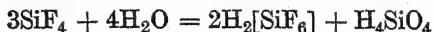
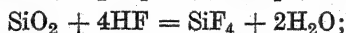
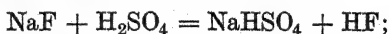
Sensitivity: 1  $\mu\text{g}$ .  $\text{I}^-$ . Concentration limit: 1 in 50,000.

## IV, 17. REACTIONS OF FLUORIDES, $\text{F}^-$

**Solubility.**—The fluorides of the common alkali metals and of silver, mercury, aluminium and nickel are readily soluble in water, those of lead, copper, ferric iron, barium and lithium are slightly soluble, and those of the alkaline earth metals are insoluble in water.

Use sodium fluoride,  $\text{NaF}$ .

**1. Concentrated Sulphuric Acid.**—With the solid fluoride, a colourless, corrosive gas, hydrogen fluoride HF, is evolved on warming; the gas fumes in moist air, and the test-tube acquires a greasy appearance as a result of the corrosive action of the vapour on the silica in the glass, which liberates the gas, silicon tetrafluoride SiF<sub>4</sub>. By holding a moistened glass rod in the vapour, gelatinous silicic acid H<sub>4</sub>SiO<sub>4</sub> is deposited on the rod; this is a product of the decomposition of the silicon tetrafluoride (compare Section VII, 17, test 8).



The same result is more readily attained by mixing the solid fluoride with an equal bulk of silica, making into a paste with concentrated sulphuric acid and warming gently; silicon tetrafluoride is readily evolved.

† The spot-test technique of the reaction utilises the conversion of the silicic and fluosilicic acids by means of ammonium molybdate into silico-molybdic acid H<sub>4</sub>[SiMo<sub>12</sub>O<sub>40</sub>]. The latter, unlike free molybdic acid, oxidises benzidine in acetic acid solution to a blue dyestuff and “molybdenum blue” is simultaneously produced.

Mix the solid test sample with a little pure silica powder in the tube of the apparatus shown in Fig. II, 6, 10 and moisten the silica with 1–2 drops of concentrated sulphuric acid. Place a drop of water on the glass knob of the stopper, insert it in position and heat the apparatus gently for about 1 minute. Remove the source of heat and allow to stand for 5 minutes. Wash the drop of water into a micro crucible, add 1–2 drops of the ammonium molybdate reagent and warm the mixture until bubbling just commences. Allow to cool, introduce a drop of a 1 per cent solution of benzidine in 10 per cent acetic acid and a few drops of saturated sodium acetate solution. A blue colour is obtained.

Sensitivity: 1 μg. F.

The ammonium molybdate reagent is prepared by dissolving 1.5 grams of ammonium molybdate in 30 ml. of water (the addition of a little ammonia solution may be necessary) and pouring into 10 ml. of nitric acid (sp. gr. 1.2).

**2. The Etching Test.**—A clean watch-glass is coated on the convex side with paraffin wax, and part of the glass is exposed by scratching a design on the wax with a nail or wire. A mixture of about 0.3 gram of the fluoride and 1 ml. of concentrated sulphuric acid is placed in a small lead or platinum crucible, and the latter immediately covered with the watch-glass, convex side down. A little water should be poured in the upper (concave) side of the watch-glass to prevent the wax

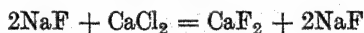
from melting. The crucible is very gently warmed (best on a boiling water bath). After 5-10 minutes, the hydrogen fluoride will have etched the glass. This is readily seen after removing the paraffin wax by holding above a flame or with hot water, and then breathing upon the surface of the glass.

The test may also be conducted in a small lead capsule, provided with a close-fitting lid made from lead foil. A small hole of about 3 mm. diameter is pierced in the lid. About 0.1 gram of the suspected fluoride and a few drops of concentrated sulphuric acid are placed in the clean capsule, and a small piece of glass (*e.g.* a microscope slide) is placed over the hole in the lid. Upon warming very gently (best on a water bath) it will be found that an etched spot appears on the glass where it covers the hole.

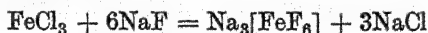
Chlorates, silicates and borates interfere and should therefore be absent.

**3. Silver Nitrate Solution:** no precipitate, since silver fluoride is soluble in water.

**4. Calcium Chloride Solution:** white, slimy precipitate of calcium fluoride  $\text{CaF}_2$ , sparingly soluble in acetic acid, but slightly more soluble in dilute hydrochloric acid.



**5. Ferric Chloride Solution:** white crystalline precipitate of the complex salt  $\text{Na}_3[\text{FeF}_6]$  from concentrated solutions of fluorides, sparingly soluble in water. The precipitate does not give the reactions of iron (*e.g.* with ammonium thiocyanate), except upon acidification.



**+6. Zirconium-Alizarin Lake Test.**—Hydrochloric acid solutions of zirconium salts are coloured reddish-violet by alizarin-S or by alizarin (see under Aluminium, Section III, 21, reactions 8 and 9, and under Zirconium, Section IX, 14, reaction 12); upon adding a solution of a fluoride the colour of such solutions changes immediately to a pale yellow (that of the liberated alizarin sulphonic acid or alizarin) because of the formation of the colourless zirconi-fluoride ion  $[\text{ZrF}_6]^{--}$ . The test may be performed on a spot plate.

Mix together on a spot plate 2 drops each (equal volumes) of a 0.1 per cent aqueous solution of alizarin-S (sodium alizarin sulphonate) and zirconyl nitrate solution (0.1 gram of the solid zirconyl nitrate dissolved in 20 ml. of concentrated hydrochloric acid and diluted to 100 ml. with water); upon the addition of a drop or two of the fluoride solution the zirconium lake is decolourised to a clear yellow solution.

Alternatively, mix 2 drops each of the alizarin-S and zirconyl nitrate solutions in a semimicro test-tube, add a drop of dilute hydrochloric acid or of 50 per cent acetic acid, followed by 2 drops of the test solution. The pink colour will change to yellow.

The most sensitive method of carrying out the spot test is as follows. Impregnate some quantitative filter paper or drop reaction paper with the zirconium-alizarin-S reagent, dry it and moisten with a drop of 50 per cent acetic acid. Place a drop of the neutral test solution upon the moist red spot; the spot will turn yellow.

Sensitivity:  $1 \mu\text{g. F}^-$ . Concentration limit: 1 in 50,000.

Large amounts of sulphates, thiosulphates, nitrites, arsenates, phosphates and oxalates interfere with the test.

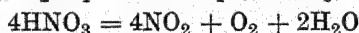
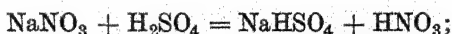
The **zirconium-alizarin-S paper** is prepared as follows. Immerse quantitative filter paper (or drop-reaction paper) in a 5 per cent solution of zirconium nitrate in 5 per cent hydrochloric acid, drain and place in a 2 per cent aqueous solution of alizarin-S. Wash the paper, which is coloured red-violet by the zirconium lake, until the washings are nearly colourless and then dry in air.

#### IV, 18. REACTIONS OF NITRATES, $\text{NO}_3^-$

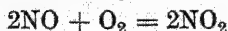
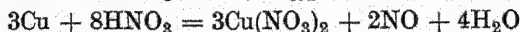
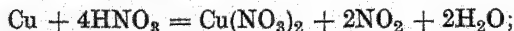
*Solubility.*—All nitrates are soluble in water. The nitrates of mercury and bismuth yield basic salts on treatment with water; these are soluble in dilute nitric acid.

Use sodium nitrate,  $\text{NaNO}_3$ .

**1. Concentrated Sulphuric Acid:** reddish-brown vapours of nitrogen dioxide, accompanied by pungent acid vapours of nitric acid which fume in the air, are formed on heating the solid nitrate with the reagent. The nitric acid initially formed is decomposed by heating. Dilute sulphuric acid has no action (difference from nitrite).



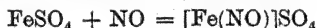
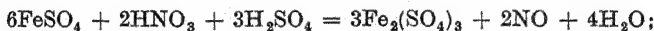
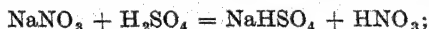
**2. Concentrated Sulphuric Acid and Bright Copper Turnings.**—On heating these with the solid nitrate, reddish-brown fumes of nitrogen dioxide are evolved, and the solution acquires a blue colour owing to the production of cupric nitrate. A solution of the nitrate may also be used; the sulphuric acid is then added very cautiously.



**3. Ferrous Sulphate Solution and Concentrated Sulphuric Acid (Brown Ring Test).**—This test is carried out in either of two ways: (a) Add 3 ml. of a freshly prepared saturated solution of ferrous sulphate to 2 ml. of the nitrate solution, and pour 3–5 ml. of concentrated sulphuric acid slowly down the side of the test-tube so that the acid forms a layer

beneath the mixture. A brown ring will form where the liquids meet. (b) Add 4 ml. of concentrated sulphuric acid slowly to 2 ml. of the nitrate solution, mix the liquids thoroughly and cool the mixture under a stream of cold water from the tap. Pour a saturated solution of ferrous sulphate slowly down the side of the tube so that it forms a layer on top of the liquid. A brown ring will form at the zone of contact of the two liquids.

The brown ring is due to the formation of the compound  $[\text{Fe}(\text{NO})]\text{SO}_4$ . On shaking and warming the mixture the brown colour disappears, nitric oxide is evolved and a yellow solution of ferric sulphate remains. The test is unreliable in the presence of bromide, iodide, nitrite, chlorate and chromate (see Section IV, 45, 3 and 4).



Bromides and iodides interfere because of the liberated halogen; the test is not trustworthy in the presence of chromates, sulphites, thiosulphates, iodates, cyanides, thiocyanates, ferro- and ferricyanides. All of these anions may be removed by adding excess of nitrate-free  $\text{Ag}_2\text{SO}_4$  to an aqueous solution (or sodium carbonate extract), shaking vigorously for 3–4 minutes, and filtering the insoluble silver salts, etc.

Nitrites react similarly to nitrates. They are best removed by adding a little sulphamic acid (compare Section IV, 7, reaction 10). The following reaction takes place in the cold:

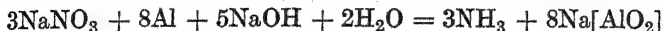
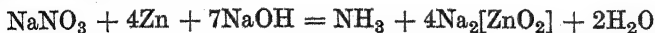


† The spot-test technique is as follows. Place a crystal of ferrous sulphate about as large as a pin head on a spot plate. Add a drop of the test solution and allow a drop of concentrated sulphuric acid to run in at the side of the drop. A brown ring forms round the crystal of ferrous sulphate.

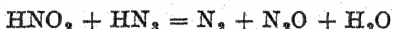
Sensitivity: 2.5  $\mu\text{g}$ .  $\text{NO}_3^-$ . Concentration limit: 1 in 25,000.

**4. Aluminium or Zinc and Sodium Hydroxide Solution (Ammonia Test).**—Ammonia is evolved (detected by its odour; by its action upon red litmus paper and upon mercurous nitrate paper; or by the tannic acid–silver nitrate test, Section III, 36, reaction 7) when a solution of a nitrate is boiled with zinc dust or gently warmed with aluminium powder and sodium hydroxide solution. Excellent results are obtained by the use of Devarda's alloy (45 per cent Al, 5 per cent Zn and 50 per cent Cu). The reduction is due to the nascent hydrogen produced in the reaction. Ammonium ions must, of course,

be removed by boiling the solution with sodium hydroxide solution (and, preferably, evaporating almost to dryness) before the addition of the metal.



Nitrites give a similar reaction and may be removed most simply with the aid of sulphamic acid (see test 3). Another, but more expensive, procedure involves the addition of sodium azide to the acid solution; the solution is allowed to stand for a short time and then boiled in order to complete the reaction and to expel the readily volatile hydrogen azide:



Other nitrogen compounds which evolve ammonia under the above conditions are cyanides, thiocyanates, ferrocyanides and ferricyanides. These may be removed by treating the aqueous solution (or a sodium carbonate extract) with excess of nitrate-free  $\text{Ag}_2\text{SO}_4$  (Compare Section IV, 45, 3), warming the mixture to about  $60^\circ$ , shaking vigorously for 3-4 minutes and filtering from the silver salts of the interfering anions and excess of precipitant. The excess of silver ions is removed from the filtrate by adding an excess of  $\text{NaOH}$  solution, and filtering from the precipitated silver oxide. The filtrate is concentrated and tested with zinc, aluminium or Devarda's alloy.

Attention is directed to the fact that arsenites are reduced in alkaline solution by aluminium, Devarda's alloy, etc., to arsine, which blackens mercurous nitrate paper and also gives a positive tannic acid-silver nitrate test. Hence neither the mercurous nitrate test nor the tannic acid-silver nitrate test for ammonia is applicable if arsenites are present.

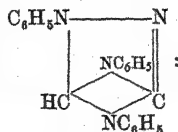
† The spot-test technique is carried out as follows. Place a drop of the test solution in the tube of Fig. II, 6, 13, add 1-2 drops of 10 per cent sodium hydroxide solution and a few milligrams of Devarda's alloy. Place a watch-glass with a drop of *p*-nitrobenzene-diazonium chloride reagent (for preparation, see under Ammonium, Section III, 36, reaction 7) on its under side upon the funnel stopper. Heat the apparatus gently for a short time. Add a tiny fragment of calcium oxide to the drop of the reagent: a red ring forms within 10-15 seconds.

Sensitivity: 10  $\mu\text{g}$ .  $\text{NO}_3^-$ . Concentration limit: 1 in 5,000.

**5. Diphenylamine Reagent ( $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ ).**—Pour the nitrate solution carefully down the side of the test-tube so that it forms a layer above the solution of the reagent; a blue ring is formed at the zone of contact of the two liquids. The test is a very sensitive one, but unfortunately is also given by a number of oxidising agents, such as nitrites, chlorates, bromates, iodates, permanganates, chromates, vanadates, molybdates and ferric salts.

The reagent is prepared by dissolving 0.5 gram of diphenylamine in 100 ml. of concentrated sulphuric acid diluted with 20 ml. of water.

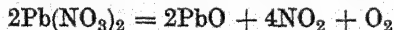
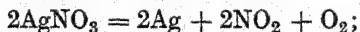
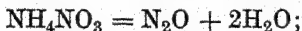
### 6. Nitron Reagent (diphenyl-endo-anilo-dihydrotriazole $C_{20}H_{16}N_4$ ),



white crystalline precipitate of nitron nitrate  $C_{20}H_{16}N_4 \cdot HNO_3$  with solutions of nitrates. Bromides, iodides, nitrites, chromates, chlorates, perchlorates, thiocyanates, oxalates and picrates also yield insoluble compounds, and hence the reaction is not very characteristic.

The reagent is prepared by dissolving 5 grams of nitron in 100 ml. of 5 per cent acetic acid.

**7. Action of Heat.**—The result varies with the metal. The nitrates of sodium and potassium evolve oxygen (test with glowing splint) and leave solid nitrites (brown fumes with dilute acid); ammonium nitrate yields nitrous oxide and steam; the nitrates of the noble metals leave a residue of the metal, and a mixture of nitrogen dioxide and oxygen is evolved; the nitrates of the other metals, such as those of lead and copper, evolve oxygen and nitrogen dioxide, and leave a residue of the oxide.



†8. **Reduction to Nitrite Test.**—Nitrates are reduced to nitrites by metallic zinc in acetic acid solution; the nitrite can be readily detected by means of the sulphanilic acid- $\alpha$ -naphthylamine reagent (see under Nitrites, Section IV, 7, reaction 11). Nitrites, of course, interfere and are best removed with sulphamic acid (see reaction 3 above).

Mix on a spot plate a drop of the neutral or acetic acid test solution with a drop of the sulphanilic acid reagent and a drop of the  $\alpha$ -naphthylamine reagent, and add a few milligrams of zinc dust. A red coloration develops.

Sensitivity: 0.05  $\mu$ g.  $NO_3^-$ . Concentration limit: 1 in 1,000,000.

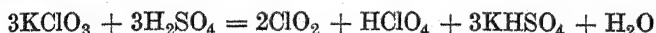
## IV, 19. REACTIONS OF CHLORATES, $ClO_3^-$

**Solubility.**—All chlorates are soluble in water; potassium chlorate is one of the least soluble (86 grams per litre at 18°) and lithium chlorate one of the most soluble (3150 grams per litre at 18°).

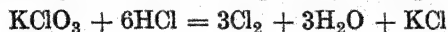
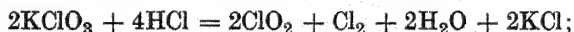
Use potassium chlorate,  $KClO_3$ .



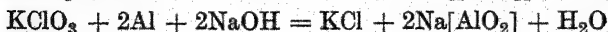
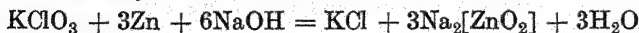
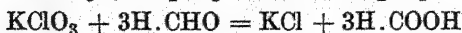
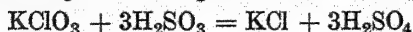
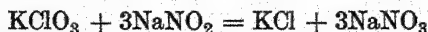
**1. Concentrated Sulphuric Acid (DANGER).**—All chlorates are decomposed with the formation of the greenish-yellow gas, chlorine dioxide  $\text{ClO}_2$ , which dissolves in the sulphuric acid to give an orange-yellow solution. On warming *gently* (DANGER) an explosive crackling occurs, which may develop into a violent explosion. In carrying out this test one or two small crystals of potassium chlorate (weighing not more than 0.1 gram) are treated with 1 ml. of concentrated sulphuric acid in the cold; the yellow explosive chlorine dioxide can be seen on shaking the solution. The test-tube should not be warmed, and its mouth should be directed away from the student.



**2. Concentrated Hydrochloric Acid.**—All chlorates are decomposed by this acid, and chlorine, together with varying quantities of the explosive chlorine dioxide, are evolved; the latter imparts a yellow colour to the acid. The mixture of gases is sometimes known as "euchlorine." The experiment should be conducted on a very small scale, not more than 0.1 gram of potassium chlorate being used. The following two chemical reactions probably occur simultaneously:



**3. Sodium Nitrite Solution.**—On warming this reagent with a solution of the chlorate, the latter is reduced to a chloride, which may be identified by adding silver nitrate solution after acidification with dilute nitric acid. The nitrite must, of course, be free from chloride. A solution of sulphurous acid or of formaldehyde (10 per cent; 1 part of formalin to 3 parts of water) acts similarly. Excellent results are obtained with zinc, aluminium or Devarda's alloy and sodium hydroxide solution (see under Nitrates, Section IV, 18, reaction 4); the solution is acidified with dilute nitric acid after several minutes boiling,\* and silver nitrate solution added.



\* It is best to filter off the excess of metal before adding the silver nitrate solution.

**4. Silver Nitrate Solution:** no precipitate in neutral solution or in the presence of dilute nitric acid. Upon the addition of a little pure (chloride-free) sodium nitrite to the dilute nitric acid solution, a white precipitate of silver chloride is obtained because of the reduction of the chlorate to chloride (see reaction 3 above).

No precipitate is obtained with barium chloride solution.

**5. Potassium Iodide Solution:** iodine is liberated if a mineral acid is present. If acetic acid is used, no iodine separates even on long standing (difference from iodate).

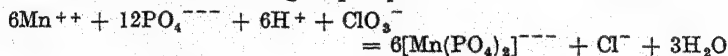
**6. Ferrous Sulphate Solution:** reduction to chloride upon boiling in the presence of dilute mineral acid (difference from perchlorate).



**7. Indigo Test.**—A dilute solution of indigo in concentrated sulphuric acid is added to the chlorate solution until the latter has a pale-blue colour. Dilute sulphurous acid or sodium sulphite solution is then added drop by drop; the blue colour is discharged. The chlorate is reduced by the sulphurous acid to chlorine or to hypochlorite, and the latter bleaches the indigo.

**8. Aniline Sulphate Test**  $\{(\text{C}_6\text{H}_5\cdot\text{NH}_2)_2\text{H}_2\text{SO}_4\}$ .—A small quantity of the solid chlorate (say,  $>0.05$  gram) (*DANGER*) is mixed with 1 ml. of concentrated sulphuric acid, and 2–3 ml. of aqueous aniline sulphate solution added; a deep-blue colour is obtained (distinction from nitrate).

**†9. Manganous Sulphate-Phosphoric Acid Test.**—Manganous sulphate in syrupy phosphoric acid solution reacts with chlorates to form the violet-coloured manganic-phosphate ion:



Persulphates, nitrites, bromates, iodates and also periodates react similarly. The first-named may be decomposed by evaporating the sulphuric acid solution with a little silver nitrate as catalyst:

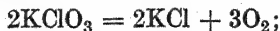


Place a drop of the test solution in a micro crucible and add a drop of the reagent. Warm rapidly over a micro burner and allow to cool. A violet coloration appears. Very pale colorations may be intensified by adding a drop of 1 per cent alcoholic diphenylcarbazine solution when a deep violet colour, due to an oxidation product of the diphenylcarbazine, is obtained.

Sensitivity:  $0.05 \mu\text{g. ClO}_3^-$ . Concentration limit: 1 in 1,000,000.

The reagent is prepared by mixing equal volumes of saturated manganous sulphate solution and syrupy phosphoric acid.

**10. Action of Heat.**—All chlorates are decomposed by heat into chlorides and oxygen. Some perchlorate is usually formed as an intermediate product. The chloride is identified in the residue by extracting with water and adding dilute nitric acid and silver nitrate solution. An insoluble chlorate should be mixed with sodium carbonate before ignition.

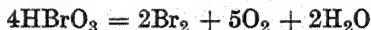


#### IV, 20. REACTIONS OF BROMATES, $\text{BrO}_3^-$

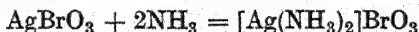
*Solubility.*—Silver, barium and lead bromates are slightly soluble in water, the solubilities being respectively 2.0 grams, 7.0 grams and 13.5 grams per litre at  $20^\circ$ ; mercurous bromate is also sparingly soluble. Most of the other metallic bromates are readily soluble in water.

Use potassium bromate,  $\text{KBrO}_3$ .

**1. Concentrated Sulphuric Acid.**—Add 2 ml. of the acid to 0.5 gram of the solid bromate; bromine and oxygen are evolved in the cold in consequence of the decomposition of the liberated bromic acid.



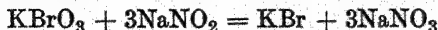
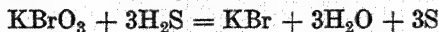
**2. Silver Nitrate Solution.**—A white crystalline precipitate of silver bromate  $\text{AgBrO}_3$  is produced with a concentrated solution of a bromate. The precipitate is soluble in hot water, readily soluble in dilute ammonia solution forming a complex salt, and difficultly soluble in dilute nitric acid.



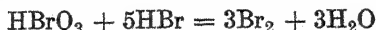
Precipitates of the corresponding bromates are also produced by the addition of solutions of barium chloride, lead acetate or mercurous nitrate to a concentrated solution of a bromate.

If the solution of silver bromate in dilute ammonia solution is treated dropwise with sulphurous acid solution, silver bromide separates: the latter dissolves in concentrated ammonia solution (difference from iodate).

**3. Sulphur Dioxide.**—If the gas is bubbled through a solution of a bromate, the latter is reduced to a bromide (see Bromides, Section IV, 15). A similar result is obtained with hydrogen sulphide and with sodium nitrite solution (see under Chlorates, Section IV, 19, reaction 3).

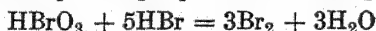


**4. Hydrobromic Acid.**—Mix together solutions of potassium bromate and bromide, and acidify with dilute sulphuric acid; bromine is liberated as a result of interaction between the bromic and hydrobromic acids set free. The bromine may be extracted by adding a little chloroform or carbon tetrachloride.



**5. Action of Heat.**—Potassium bromate on heating evolves oxygen and a bromide remains. No perbromate is formed. Sodium and calcium bromates behave similarly, but cobalt, zinc and other similar metallic bromates evolve oxygen and bromine, and leave an oxide.

**6. Manganous Sulphate Test.**—If a bromate solution is treated with a little of a 1 : 1 mixture of saturated manganous sulphate solution and 2*N* sulphuric acid, a transient red coloration (due to manganic sulphate) is observed. Upon concentrating the solution rapidly, brown hydrated manganese dioxide separates. The latter is insoluble in dilute sulphuric acid, but dissolves in a mixture of dilute sulphuric and oxalic acids (difference from chlorates and iodates, which neither give the coloration nor yield the brown precipitate).



† In the spot test technique, the reaction is combined with a sensitive test for manganese (oxidation of benzidine by manganese dioxide to "benzidine blue"). Place a drop of the test solution in a semimicro centrifuge tube, add a drop or two of 2 per cent manganous sulphate solution acidified with dilute sulphuric acid and warm for 2-3 minutes in a boiling water bath. Cool, add a few drops of the benzidine reagent and a few small crystals of sodium acetate. A blue coloration results.

Sensitivity: 30  $\mu\text{g}$ .  $\text{BrO}_3^-$ . Concentration limit: 1 in 2500.

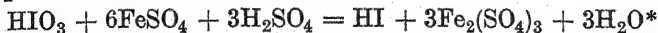
The benzidine reagent is prepared by dissolving 0.05 gram of benzidine in 10 ml. of acetic acid, diluting to 100 ml. with water and filtering, if necessary.

## IV, 21. REACTIONS OF IODATES, $\text{IO}_3^-$

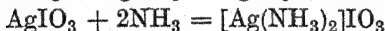
**Solubility.**—The iodates of the alkali metals are soluble in water; those of the other metals are sparingly soluble and, in general, less soluble than the corresponding chlorates and bromates. Some solubilities in grams per litre at 20° are: lead iodate 0.03 (25°), silver iodate 0.06, barium iodate 0.22, calcium iodate 3.7, potassium iodate 81.3 and sodium iodate 90.0. Iodic acid is a crystalline solid, and has a solubility of 2330 grams per litre at 20°.

Use potassium iodate,  $\text{KIO}_3$ .

1. **Concentrated Sulphuric Acid:** no action in the absence of reducing agents; readily converted into hydriodic acid in the presence of ferrous sulphate.



2. **Silver Nitrate Solution:** white, curdy precipitate of silver iodate  $\text{AgIO}_3$ , readily soluble in dilute ammonia solution, but difficultly soluble in dilute nitric acid.

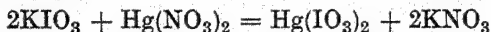


If the ammoniacal solution of the precipitate is treated dropwise with sulphurous acid solution, silver iodide is precipitated; the latter is not dissolved by concentrated ammonia solution (difference from bromate).

3. **Barium Chloride Solution:** white precipitate of barium iodate  $\text{Ba}(\text{IO}_3)_2$  (difference from chlorate), difficultly soluble in hot water and in dilute nitric acid, but insoluble in alcohol (difference from iodide). If the precipitate of barium iodate is well washed, treated with a little sulphurous acid solution and 1-2 ml. of carbon tetrachloride, the latter is coloured violet by the liberated iodine.

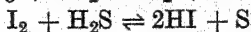
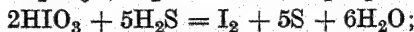
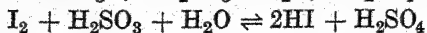
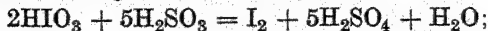
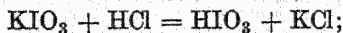


4. **Mercuric Nitrate Solution:** white precipitate of mercuric iodate  $\text{Hg}(\text{IO}_3)_2$  (difference from chlorate and bromate). Lead acetate solution similarly gives a precipitate of lead iodate  $\text{Pb}(\text{IO}_3)_2$ .



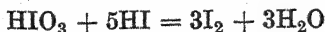
Mercuric chloride solution, which is practically unionised (as mercuric chloride is covalent), gives no precipitate.

5. **Sulphur Dioxide or Hydrogen Sulphide.**—Passage of sulphur dioxide or of hydrogen sulphide into a solution of an iodate, acidified with dilute hydrochloric acid, liberates iodine, which may be recognised by the addition of starch solution or chloroform or carbon tetrachloride. With an excess of either reagent, the iodine is further reduced to hydriodic acid.

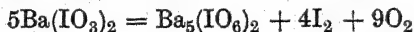
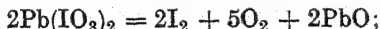
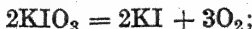


\* Iodine will eventually separate owing to the interaction between the hydriodic and iodic acid (see reaction 6 below).

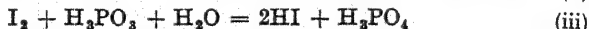
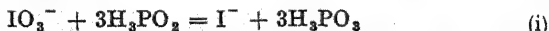
**6. Potassium Iodide Solution.**—Mix together solutions of potassium iodide and potassium iodate, and acidify with acetic acid or with tartaric acid solution; iodine is immediately liberated (use the chloroform or carbon tetrachloride test).



**7. Action of Heat.**—The alkali iodates decompose into oxygen and an iodide. Most iodates of the divalent metals yield iodine and oxygen and leave a residue of oxide; barium iodate, exceptionally, gives the periodate.



**†8. Hypophosphorous Acid-Starch Solution Test.**—Iodates are reduced by hypophosphorous acid eventually to iodides. The reaction takes place in three stages:

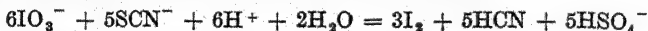


The first two stages are rapid and the third stage is a slow reaction. The iodine can be readily identified by the starch reaction. Chlorates and bromates do not react under these conditions.

Place a drop of the neutral test solution on a spot plate and mix it with a drop of starch solution (for preparation, see under Iodides, Section IV, 16, reaction 9) and a drop of a dilute solution of hypophosphorous acid. A transitory blue coloration is produced.

Sensitivity:  $1 \mu\text{g. IO}_3^-$ . Concentration limit: 1 in 50,000.

**†9. Potassium Thiocyanate Test.**—Iodates react with thiocyanates in acid solution with the liberation of iodine:



Treat a piece of starch paper successively with a drop of 5 per cent potassium thiocyanate solution and a drop of the acid test solution. A blue spot is obtained.

Sensitivity:  $3 \mu\text{g. IO}_3^-$ . Concentration limit: 1 in 12,000.

## IV, 22. REACTIONS OF PERCHLORATES, $\text{ClO}_4^-$

**Solubility.**—The perchlorates are generally soluble in water. Potassium perchlorate is one of the least soluble (7.5 grams and 218 grams per litre at  $0^\circ$  and  $100^\circ$  respectively), and sodium perchlorate is one of the most soluble (2096 grams per litre at  $25^\circ$ ).

Use sodium perchlorate,  $\text{NaClO}_4$ .

**1. Concentrated Sulphuric Acid:** no visible action with the solid salt although the free perchloric acid  $\text{HClO}_4$  is

liberated; on strong heating, white fumes of the hydrate,  $\text{HClO}_4 \cdot \text{H}_2\text{O}$ , are evolved.



**2. Potassium Chloride Solution:** white precipitate of potassium perchlorate  $\text{KClO}_4$ , insoluble in alcohol (see under Potassium, Section III, 34, reaction 3). Ammonium chloride solution gives a similar white precipitate of ammonium perchlorate  $\text{NH}_4\text{ClO}_4$ .

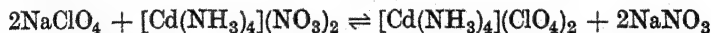
**3. Barium Chloride Solution:** no precipitate. A similar result is obtained with silver nitrate solution.

**4. Indigo Test:** no decolourisation even in the presence of acid (difference from hypochlorite and chlorate).

**5. Sulphur Dioxide or Hydrogen Sulphide or Ferrous Salts:** no reduction (difference from chlorate).

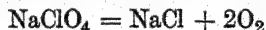
**6. Titanous Sulphate Solution:** reduced to chloride.

**7. Cadmium Ammonium Perchlorate Test.**—When a solution of a perchlorate is treated with a saturated solution of cadmium nitrate in concentrated ammonia solution, a white crystalline precipitate of cadmium ammonium perchlorate is obtained.



Sulphides interfere and should therefore be absent.

**8. Action of Heat:** oxygen is evolved, and a chloride (for tests see under Chlorides, Section IV, 14) is produced.

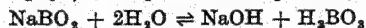
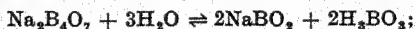


#### IV, 23.

#### REACTIONS OF BORATES,



The borates are derived from the three boric acids: ortho-boric acid  $\text{H}_3\text{BO}_3$ , pyro-boric acid  $\text{H}_2\text{B}_4\text{O}_7$ , and meta-boric acid  $\text{HBO}_2$ . Ortho-boric acid is a white crystalline solid, sparingly soluble in cold but more soluble in hot water; very few salts of this acid are definitely known. On heating ortho-boric acid at  $100^\circ$ , it is converted into meta-boric acid; at  $140^\circ$  pyro-boric acid is produced. Most of the salts are derived from the meta- and pyro-acids. Owing to the weakness of boric acid, the soluble salts are hydrolysed in solution and therefore react alkaline.



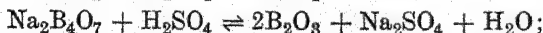
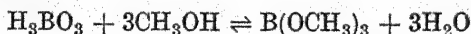
**Solubility.**—The borates of the alkali metals are readily soluble in water. The borates of the other metals are, in general, difficultly soluble in water, but fairly soluble in acids and in ammonium chloride solution.

Use sodium pyro-borate ("borax"),  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ .

**1. Concentrated Sulphuric Acid:** no visible action in the cold, although ortho-boric acid  $\text{H}_3\text{BO}_3$  is set free. On heating, however, white fumes of boric acid are evolved. If concentrated hydrochloric acid is added to a concentrated solution of borax, boric acid is precipitated.



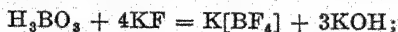
**2. Concentrated Sulphuric Acid and Alcohol (Flame Test).**—If a little borax is mixed with 1 ml. of concentrated sulphuric acid and 5 ml. of methyl or ethyl alcohol (the former is to be preferred owing to its greater volatility) in a small porcelain basin, and the alcohol ignited, the latter will burn with a green-edged flame, due to the formation of methyl borate  $\text{B}(\text{OCH}_3)_3$  or of ethyl borate  $\text{B}(\text{OC}_2\text{H}_5)_3$ . Both these esters are poisonous. Copper and barium salts may give a similar green flame. The following modification of the test, which depends upon the greater volatility of boron trifluoride  $\text{BF}_3$ , can be used in the presence of copper and barium compounds; these do not form volatile compounds under the experimental conditions given below. Thoroughly mix the borate with powdered calcium fluoride and a little concentrated sulphuric acid, and bring a little of the paste thus formed on the loop of a platinum wire, or upon the end of a glass rod, very close to the edge of the base of a Bunsen flame without actually touching it; volatile boron trifluoride is formed and colours the flame green.



† The reaction may be adapted as a spot test in the following manner. The methyl borate is distilled off and passed into an aqueous solution containing potassium fluoride, manganous nitrate and silver nitrate. The ester is hydrolysed by the water to boric acid:



the boric acid reacts with the alkali fluoride forming a borofluoride and liberating free caustic alkali:



the free caustic alkali is identified by the formation of a black precipitate with manganous nitrate-silver nitrate solution (see under Ammonium, Section III, 36, reaction 9):





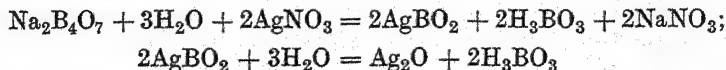
Place a drop of the alkaline test solution in the distillation apparatus of Fig. II, 6, 16 and evaporate to dryness. Add 5 drops of concentrated sulphuric acid and 5 drops of pure methyl alcohol, stopper the apparatus and heat to  $80^{\circ}\text{C}$  in a water bath. Collect the methyl borate which distills over in a micro porcelain crucible, waxed on the inside, and containing about 1 ml. of the reagent. A black precipitate forms. For very small amounts of borate it is best to add a few drops of benzidine acetate solution and thus to detect the traces of manganese dioxide by the resulting blue colour.

Sensitivity: 0.01  $\mu\text{g}$ . B. Concentration limit: 1 in 5,000,000.

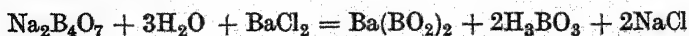
The reagent (a manganous nitrate-silver nitrate solution containing potassium fluoride) is prepared as follows. Dissolve 2.87 grams of manganous nitrate and 1.69 grams of silver nitrate in 100 ml. of water, add a drop of dilute alkali and filter the solution from the black precipitate. Treat the filtrate with a solution of 3.5 grams of potassium fluoride in 50 ml. of water; a white precipitate will form which on heating becomes grey and black. Boil, filter and use the clear solution as the reagent.

**3. Turmeric Paper Test.**—If a piece of turmeric paper is dipped into a solution of a borate acidified with dilute hydrochloric acid and then dried at  $100^{\circ}$ , it becomes reddish-brown. The drying of the paper is most simply carried out by winding it on the outside near the rim of a test-tube containing water, and boiling the water for 2–3 minutes. On moistening the paper with dilute sodium hydroxide solution, it becomes bluish-black or greenish-black. Chromates, chlorates, nitrites, iodides and other oxidising agents interfere because of their bleaching action on the turmeric.

**4. Silver Nitrate Solution:** white precipitate of silver metaborate  $\text{AgBO}_2$  from fairly concentrated borax solution, soluble in both dilute ammonia solution and in acetic acid. On boiling the precipitate with water, it is completely hydrolysed and a brown precipitate of silver oxide is obtained. A brown precipitate of silver oxide is produced directly in very dilute solutions.

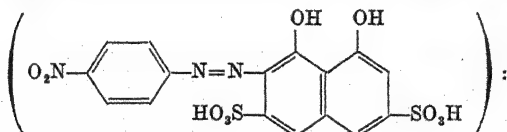


**5. Barium Chloride Solution:** white precipitate of barium meta-borate  $\text{Ba}(\text{BO}_2)_2$  from fairly concentrated solutions; the precipitate is soluble in excess of the reagent, in dilute acids and in solutions of ammonium salts. Solutions of calcium and strontium chloride behave similarly.



**6. Action of Heat.**—Powdered borax when heated in an ignition tube, or upon a platinum wire, swells up considerably, and then subsides, leaving a colourless glass of the anhydrous salt. The glass possesses the property of dissolving many oxides on heating, forming meta-borates, which often have characteristic colours. This is the basis of the borax bead test for various metals (see Section II, 1, reaction 5).

†7. **para-Nitrobenzene-azo-chromotropic Acid\* Reagent**



Borates cause the blue-violet reagent to assume a greenish-blue colour.

Evaporate a drop of the slightly alkaline solution to dryness in a semimicro crucible. Stir the warm residue with 2–3 drops of the reagent. A greenish-blue coloration is obtained on cooling. A blank test should be performed simultaneously.

Sensitivity: 0.1  $\mu\text{g}$ . B. Concentration limit: 1 in 500,000.

Oxidising agents and fluorides interfere, the latter because of the formation of borofluorides. Oxidising agents, including nitrates and chlorates, are rendered innocuous by evaporating with solid hydrazine sulphate, whilst fluorides may be removed as silicon tetrafluoride by evaporation with silicic acid and sulphuric acid.

The experimental details are as follows. Treat 2 drops of the test solution in a small porcelain crucible either with a little solid hydrazine sulphate or with a few specks of precipitated silica and 1–2 drops of concentrated sulphuric acid, and heat cautiously until fumes of sulphuric acid appear. Add 3–4 drops of the reagent whilst the residue is still warm and observe the colour on cooling.

Sensitivity: 0.25  $\mu\text{g}$ . B in the presence of 12,000 times the amount of  $\text{KClO}_3$  or  $\text{KNO}_3$ ; 0.5  $\mu\text{g}$ . B in the presence of 2,500 times the amount of  $\text{NaF}$ .

The reagent consists of a 0.005 per cent solution of Chromotrope 2B in concentrated sulphuric acid.

†8. **Mannitol-Bromothymol Blue Test.**—Boric acid acts as a very weak monobasic acid ( $K_a = 5.8 \times 10^{-10}$ ), but upon the additions of certain organic poly-hydroxy compounds, such as mannitol (mannite), glycerol, dextrose or invert sugar, it is transformed into a relatively strong acid, probably of the type:



\* Alternative names are: *p*-nitrobenzene-azo-1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid and "Chromotrope 2B" (the latter is the sodium salt).

The pH of the solution therefore decreases. Hence if the solution is initially almost neutral to, say, bromothymol blue (green), then upon the addition of mannitol the colour becomes yellow. It is advisable when testing for minute quantities of borates to recrystallise the mannitol from a solution neutralised to bromothymol blue, wash with pure acetone and dry at 100°. The reagent (a 10 per cent aqueous solution of mannitol) may also be neutralised with 0.01N potassium hydroxide solution, using bromothymol blue (a 0.04 per cent solution in 96 per cent ethyl alcohol) as indicator. Only periodate interferes with the test: it can be decomposed by heating on charcoal.

Render the test solution almost neutral to bromothymol blue by treating it with dilute acid or alkali (as necessary) until the indicator turns green. Place a few drops of the test solution in a micro test-tube, and add a few drops of the reagent solution. A yellow coloration is obtained in the presence of a borate. It is advisable to carry out a blank test with distilled water simultaneously.

Sensitivity: 0.001 µg. B. Concentration limit: 1 in 30,000,000.

#### IV, 24. REACTIONS OF SULPHATES, $\text{SO}_4^{--}$

*Solubility.*—The sulphates of barium, strontium and lead are practically insoluble in water,\* those of calcium and mercuric mercury are slightly soluble, and most of the remaining metallic sulphates are soluble. Some basic sulphates, such as those of mercury, bismuth and chromium, are also insoluble in water, but these dissolve in dilute hydrochloric or nitric acid.

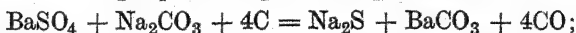
Sulphuric acid is a colourless, oily and hygroscopic liquid, of specific gravity 1.838. The pure, commercial, concentrated acid is a constant boiling point mixture, boiling point 338° and containing ca. 98 per cent of acid. It is miscible with water in all proportions with the evolution of considerable heat; on mixing the two, the acid should always be poured in a thin stream into the water (if the water is poured into the heavier acid, steam may be suddenly generated which will carry with it some of the acid and may therefore cause considerable damage).

Use sodium sulphate,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ .

**1. Barium Chloride Solution:** white precipitate of barium sulphate  $\text{BaSO}_4$  (see under Barium, Section III, 29), insoluble in warm dilute hydrochloric acid and in dilute nitric acid, but moderately soluble in boiling, concentrated hydrochloric acid. The test is usually carried out by adding the reagent to the solution acidified with dilute hydrochloric acid; carbonates, sulphites and phosphates are not precipitated under these conditions. Concentrated hydrochloric acid or concentrated nitric acid should not be used, as a precipitate of barium chloride or of barium nitrate may form; these dissolve, however, upon dilution with water. The barium sulphate precipitate may be filtered from the hot solution and fused on charcoal with sodium carbonate, when sodium sulphide will be formed. The latter may be extracted with water, and the extract filtered into a freshly prepared solution of sodium nitroprusside, when

\* Of these three sulphates, that of strontium is the most soluble.

a transient, purple coloration is obtained (see under Sulphides, Section IV, 6, reaction 5). An alternative method is to add a few drops of very dilute hydrochloric acid to the fused mass, and to cover the latter with lead acetate paper; a black stain of lead sulphide is produced on the paper. The so-called **Hepar reaction**, which is less sensitive than the above two tests, consists in placing the fusion product on a silver coin and moistening with a little water; a brownish-black stain of silver sulphide results.



A more efficient method for decomposing most sulphur compounds consists in heating them with sodium or potassium, and then testing the solution of the product for sulphide. The test is rendered sensitive by heating the substance with potassium in an ignition tube, dissolving the melt in water, and testing for sulphide by the nitroprusside or methylene blue reactions (see under Sulphides, Section IV, 6, reactions 6 and 7).

The reader is warned that the above tests (depending upon the formation of a sulphide) are not exclusive to sulphates but are given by most sulphur compounds. If, however, the barium sulphate precipitated in the presence of hydrochloric acid is employed, then the reaction may be employed as a confirmatory test for sulphates.

**2. Lead Acetate Solution:** white precipitate of lead sulphate  $\text{PbSO}_4$ , soluble in hot concentrated sulphuric acid, in solutions of ammonium acetate and of ammonium tartrate (see under Lead, Section III, 2, reaction 3), and in sodium hydroxide solution. In the last case sodium plumbite is formed, and on acidification with hydrochloric acid, the lead crystallises out as the chloride. If any of the aqueous solutions of the precipitate are acidified with acetic acid and potassium chromate solution added, yellow lead chromate is precipitated (see under Lead, *loc. cit.*).



**3. Silver Nitrate Solution:** white, crystalline precipitate of silver sulphate  $\text{Ag}_2\text{SO}_4$  (solubility 5.8 grams per litre at  $18^\circ$ ) from concentrated solutions.



† **4. Sodium Rhodizonate Test.**—Barium salts yield a reddish-brown precipitate with sodium rhodizonate (see under Barium, Section III, 29,

reaction 7). Sulphates and sulphuric acid cause immediate decolorisation because of the formation of insoluble barium sulphate. This test is specific for sulphates.

Place a drop of barium chloride solution upon filter or drop reaction paper, followed by a drop of a freshly prepared 0.1 per cent aqueous solution of sodium rhodizonate. Treat the reddish-brown spot with a drop of the acid or alkaline test solution. The coloured spot disappears.

Sensitivity: 4  $\mu\text{g}$ .  $\text{SO}_4^{--}$ . Concentration limit: 1 in 10,000.

†5. **Potassium Permanganate-Barium Sulphate Test.**—If barium sulphate is precipitated in a solution containing potassium permanganate, it is coloured pink (violet) by adsorption of some of the permanganate. The permanganate which has been adsorbed on the precipitate cannot be reduced by the common reducing agents (including hydrogen peroxide); the excess of potassium permanganate in the mother liquor reacts readily with reducing agents, thus rendering the pink barium sulphate clearly visible in the colourless solution.

Place 3 drops of the test solution in a semimicro centrifuge tube, add 2 drops of 1 per cent potassium permanganate solution and 1 drop of 1 per cent barium chloride solution. A pink precipitate is obtained. Add a few drops of 3 per cent hydrogen peroxide solution or *N* oxalic acid solution (in the latter case it will be necessary to warm on a water bath until decolourisation is complete). Centrifuge: the coloured precipitate is clearly visible.

Sensitivity: 2.5  $\mu\text{g}$ .  $\text{SO}_4^{--}$ . Concentration limit: 1 in 20,000.

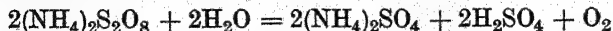
6. **Mercuric Nitrate Solution:** yellow precipitate of the basic sulphate,  $3\text{HgO} \cdot \text{SO}_3$ . This is a sensitive test, and is given by barium and lead sulphates.

#### IV, 25. REACTIONS OF PERSULPHATES, $\text{S}_2\text{O}_8^{--}$

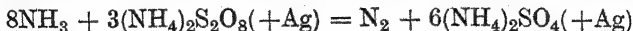
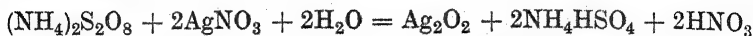
*Solubility.*—The best-known persulphates, those of sodium, potassium, ammonium and barium, are soluble in water, the potassium salt being the least soluble (17.7 grams per litre at  $0^\circ$ ).

Use ammonium persulphate,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ .

1. **Water.**—All persulphates are decomposed on boiling with water into the sulphate, free sulphuric acid and oxygen. The oxygen contains appreciable quantities of ozone, which may be detected by its odour or by its property of turning starch-iodide paper blue. A similar result is obtained with dilute sulphuric or nitric acid. With dilute hydrochloric acid, chlorine is evolved (see reaction 4 below). By dissolving the solid persulphate in concentrated sulphuric acid at  $0^\circ$ , permonosulphuric acid (Caro's acid)  $\text{H}_2\text{SO}_5$  is formed in solution; this possesses strong oxidising properties.

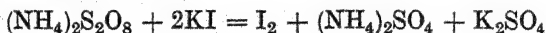


**2. Silver Nitrate Solution:** black precipitate of silver peroxide  $\text{Ag}_2\text{O}_2$  from concentrated solutions. If only a little silver nitrate solution be added and then dilute ammonia solution, the silver peroxide, or the silver ion, acts catalytically leading to the evolution of nitrogen and the liberation of considerable heat.

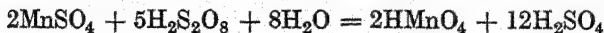
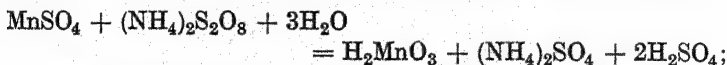


**3. Barium Chloride Solution:** no immediate precipitate in the cold with a solution of a pure persulphate; on standing for some time or on boiling, a precipitate of barium sulphate is obtained, due to the decomposition of the persulphate.

**4. Potassium Iodide Solution:** iodine is *slowly* liberated in the cold and rapidly on warming (test with starch solution) (distinction from **perborate** and **percarbonate**, which liberate iodine immediately). Ferrous sulphate solution is oxidised to ferric sulphate.



**5. Manganous Sulphate Solution:** brown precipitate,  $\text{MnO}_2 \cdot \text{H}_2\text{O}$  or  $\text{H}_2\text{MnO}_3$ , in neutral or preferably alkaline (sodium hydroxide) solution. In nitric acid solution and in the presence of a little silver nitrate (which acts catalytically, see reaction 2 above), permanganic acid is formed on warming.



**6. Potassium Permanganate Solution:** unaffected (distinction from hydrogen peroxide). Persulphates are unaffected by a solution of titanous sulphate.

**†7. Benzidine Acetate Test.**—A neutral or a weakly acetic acid solution of a persulphate converts benzidine into a blue oxidation product. Alkali perborates, percarbonates and also hydrogen peroxide do not give the test. Chromates, ferricyanides, permanganates and hypohalides react similarly to persulphates.

Mix 1 drop of the test solution (neutral or faintly acid with acetic acid) with 1 drop of the benzidine acetate reagent. A blue coloration is produced.

Sensitivity:  $1 \mu\text{g. S}_2\text{O}_8^{--}$ . Concentration limit: 1 in 100,000.

The reagent consists of a 2 per cent solution of benzidine in dilute acetic acid.

# IV, 26. REACTIONS OF SILICATES, $\text{SiO}_3^{--}$

The silicic acids may be represented by the general formula  $x\text{SiO}_2, y\text{H}_2\text{O}$ . Salts corresponding to ortho-silicic acid  $\text{H}_2\text{SiO}_4 (\text{SiO}_2, 2\text{H}_2\text{O})$  meta-silicic acid  $\text{H}_2\text{SiO}_3 (\text{SiO}_2, \text{H}_2\text{O})$  and di-silicic acid  $\text{H}_4\text{Si}_2\text{O}_5 (2\text{SiO}_2, \text{H}_2\text{O})$  are definitely known. The meta-silicates are sometimes designated simply as silicates.

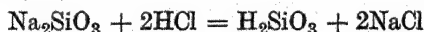
*Solubility.*—Only the silicates of the alkali metals are soluble in water; they are hydrolysed in aqueous solution and therefore react alkaline.



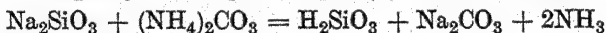
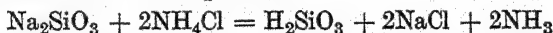
Use a solution of water glass; this contains, largely, sodium meta-silicate  $\text{Na}_2\text{SiO}_3$ .

**1. Dilute Hydrochloric Acid.**—Add dilute hydrochloric acid to the solution of the silicate; a gelatinous precipitate of meta-silicic acid is obtained, particularly on boiling. The precipitate is insoluble in concentrated acids. The freshly precipitated substance is appreciably soluble in water and in dilute acids. It is converted by repeated evaporation with concentrated hydrochloric acid on the water bath into a white insoluble powder (silica  $\text{SiO}_2$ ).

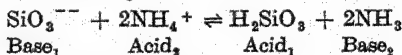
If a dilute solution (say, 1–10 per cent) of water glass is quickly added to moderately concentrated hydrochloric acid, no precipitation of silicic acid takes place; it remains in colloidal solution (sol).



**2. Ammonium Chloride or Ammonium Carbonate Solution:** gelatinous precipitate of silicic acid. This reaction is important in routine qualitative analysis since silicates, unless previously removed, will be precipitated by ammonium chloride solution in Group IIIA.

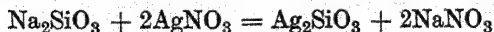


The reaction is essentially:



The  $\text{NH}_4^+$  ion functions as an acid.

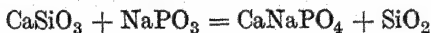
**3. Silver Nitrate Solution:** yellow precipitate of silver silicate  $\text{Ag}_2\text{SiO}_3$ , soluble in dilute acids and in dilute ammonia solution.



**4. Barium Chloride Solution:** white precipitate of barium silicate  $\text{BaSiO}_3$ , soluble in dilute nitric acid. Calcium chloride solution gives a similar precipitate of calcium silicate.

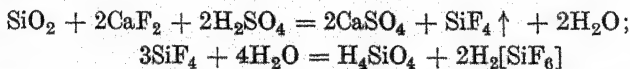


**5. Microcosmic Salt Bead Test.**—Most silicates, and also silica, when fused in a bead of microcosmic salt,  $\text{Na}(\text{NH}_4)\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ , in a loop of platinum wire give this test. The microcosmic salt first fuses to a transparent bead consisting largely of sodium meta-phosphate (see Section II, 1, reaction 6); when a minute quantity of the solid silicate or even of the solution is introduced into the bead (best by dipping the hot bead into the substance) and the whole again heated, the silica produced will not dissolve in the bead, but will swim about in the fused mass, and is visible as white opaque masses or “skeletons” in both the fused and the cold bead.



**Insoluble silicates** are best brought into solution by fusing the powdered solid, mixed with 6 times its weight of fusion mixture, in a platinum crucible\* or upon platinum foil; the alkali carbonates react with the silicate yielding an alkali silicate. The cold mass is then evaporated to dryness on the water bath with excess of dilute hydrochloric acid; the alkali silicate is thereby first decomposed yielding gelatinous silicic acid and ultimately into white, amorphous silica, whilst the metallic oxides derived from the insoluble silicate are converted into chlorides. The residue is extracted with boiling dilute hydrochloric acid; this removes the metals as chlorides and insoluble silica remains behind. A simpler, but not quantitative, method is to extract the fusion mixture melt with boiling water: sufficient sodium or potassium silicate passes into solution to give any of the reactions referred to above.

**6. Silicon Tetrafluoride Test.**—This test depends upon the fact that when silica (isolated from a silicate by treatment with ammonium chloride solution or with hydrochloric acid, etc.) is heated with defect of calcium fluoride and some concentrated sulphuric acid, silicon tetrafluoride is evolved. The latter is identified by its action upon a drop of water held in a loop of platinum wire, when a turbidity (due to silicic acid) is produced.



Excess of calcium fluoride should be avoided since a mixture of  $\text{HF}$  and  $\text{SiF}_4$  will be formed and interfere with the test.

Mix the solid substance (or, preferably, silicic acid isolated by treatment of the silicate with ammonium chloride solution) with one-third of its weight of calcium fluoride in a small lead (or platinum) capsule, and add sufficient concentrated sulphuric acid to form a thin paste: mix the contents of the capsule with a stout platinum wire. Warm gently [*FUME CUPBOARD*]

\* A nickel or iron crucible should be used if metals of Group I or II are likely to be present.



and hold close above the mixture a loop of platinum wire supporting a drop of water. The drop of water will become turbid, due to the hydrolysis of the silicon tetrafluoride absorbed.

†7. **Ammonium Molybdate-Benzidine Test.**—Silicates react with molybdates in acid solution to form the complex silico-molybdic acid  $H_4[SiMo_{12}O_{40}]$ , of which the ammonium salt, unlike the analogous phosphoric acid and arsenic acid compounds, is soluble in water and acids to give a yellow solution. The test depends upon the reaction between silico-molybdic acid and benzidine in acetic acid solution whereby "molybdenum blue" and a blue quinonoid oxidation compound of benzidine are produced.

Place a drop of the test solution and of the molybdate reagent upon drop reaction paper, and warm gently over a wire gauze. Add a drop of the benzidine reagent and hold the paper over ammonia vapour. A blue coloration results.

Sensitivity: 1  $\mu g.$   $SiO_2$ . Concentration limit: 1 in 50,000.

A better method for conducting the test is the following. Place a drop of the slightly acid test solution (the acidity should not exceed 0.5N) in a small porcelain crucible of good quality, and add a drop of the molybdate reagent. Warm cautiously over a wire gauze (or upon a sheet of asbestos resting upon a hot plate) until bubbles escape. Cool, add a drop of the benzidine reagent followed by a drop of saturated sodium acetate solution. A blue colour is obtained. It is essential to carry out a blank test with a drop of water and a drop of the molybdate reagent in another crucible of similar quality.

Sensitivity: 0.1  $\mu g.$   $SiO_2$ . Concentration limit: 1 in 500,000.

Phosphoric and arsenic acids form compounds analogous to silico-molybdic acid which also react with benzidine with colour formation hence these acids should be removed before applying the test. In the presence of phosphoric acid, the test is carried out as follows. Mix a drop of the test solution with 2 drops of the molybdate reagent in a micro centrifuge tube and centrifuge the mixture. Transfer the supernatant liquid to a micro-crucible by means of a capillary tube, warm gently, cool and add 2 drops of 1 per cent oxalic acid solution (the latter decomposes the small quantity of residual phosphomolybdate  $(NH_4)_3[PMo_{12}O_{40}]$  but has little action on the silico-molybdic acid complex), then introduce a drop of the benzidine reagent and 2-3 drops of saturated sodium acetate solution. A blue colour forms.

Sensitivity: 6  $\mu g.$   $SiO_2$  in the presence of 250 times the amount of  $P_2O_5$ . Concentration limit: 1 in 8,000.

The ammonium molybdate reagent is prepared by dissolving 5 grams of ammonium molybdate in 100 ml. of cold water and pouring into 35 ml. of nitric acid (sp. gr. 1.2).

The benzidine reagent is made by dissolving 0.05 gram of benzidine or its hydrochloride in 10 ml. of glacial acetic acid and diluting with water to 100 ml.

†8. **Ammonium Molybdate-Stannous Chloride Test.**—The silicate is separated by volatilisation as silicon tetrafluoride and the

latter collected in a little sodium hydroxide solution. The resulting silicate is treated with ammonium molybdate solution and the ammonium salt of silicomolybdic acid  $H_4[SiMo_{12}O_{40}]$  is reduced by stannous chloride solution to "molybdenum blue." Stannous chloride does not reduce ammonium molybdate solution.

Phosphates and arsenates give the same reaction, but do not interfere under the conditions of the test: large amounts of borates should be absent, but may be removed by warming with methyl alcohol and sulphuric acid.

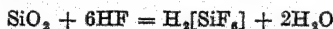
Place a little of the solid silicate in a small lead or platinum crucible, add a little sodium fluoride and a few drops of concentrated sulphuric acid. Cover the crucible with a small sheet of cellophane from which is suspended a drop of 2*N* sodium hydroxide solution (freshly prepared from the A.R. solid). Warm *gently* for 3–5 minutes over a micro burner with the crucible about 8 cm. from the flame. Transfer the drop of sodium hydroxide solution to a micro porcelain crucible, add 2 drops of a freshly prepared 10 per cent aqueous solution of ammonium molybdate and then 4*N* acetic acid until feebly acidic. Then add a few drops of a 5 per cent solution of stannous chloride in 3*N* hydrochloric acid, followed by sufficient sodium hydroxide solution to dissolve the stannous hydroxide. A blue coloration is obtained.

Concentration limit: 1 in 10,000.

The reaction may be applied to aqueous solutions of silicates, but phosphates and arsenates must be absent.

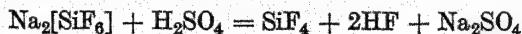
#### IV, 27. REACTIONS OF SILICOFLUORIDES (FLUOSILICATES), $[SiF_6]^{--}$

*Solubility.*—Most metallic silicofluorides, with the exception of the barium and potassium salts which are sparingly soluble, are soluble in water. A solution of the acid (hydrofluosilicic acid  $H_2[SiF_6]$ ) is one of the products of the action of water upon silicon tetrafluoride, and is also formed by dissolving silica in hydrofluoric acid.



Use sodium silicofluoride or ammonium silicofluoride.

**1. Concentrated Sulphuric Acid:** silicon fluoride and hydrogen fluoride are evolved on warming the reagent with the solid salt. If the reaction is carried out in a platinum or lead capsule or crucible, the escaping gas will etch glass and will cause a drop of water to become turbid (see under Silicates, Section IV, 26, reaction 6).



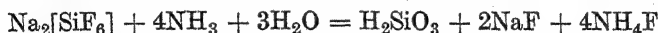
**2. Barium Chloride Solution:** white, crystalline precipitate of barium silicofluoride  $Ba[SiF_6]$ , sparingly soluble in water (0.25 gram per litre at 25°) and insoluble in dilute hydrochloric acid. The precipitate is distinguished from barium sulphate by the evolution of hydrogen fluoride and silicon fluoride,

which etch glass, on heating with concentrated sulphuric acid in a lead crucible.

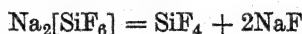


**3. Potassium Chloride Solution:** white, gelatinous precipitate of potassium silicofluoride  $\text{K}_2[\text{SiF}_6]$  from concentrated solutions. The precipitate is slightly soluble in water (1.77 grams per litre at  $25^\circ$ ), less soluble in excess of the reagent and in 50 per cent alcohol.

**4. Ammonia Solution:** decomposition occurs with the separation of gelatinous silicic acid.



**5. Action of Heat:** decomposition occurs into silicon tetrafluoride, which renders a drop of water turbid, and the metallic fluoride, which can be tested for in the usual manner (see under Fluorides, Section IV, 17).



## IV, 28. REACTIONS OF ORTHOPHOSPHATES,



Three phosphoric acids are known: ortho- $\text{H}_3\text{PO}_4$ , pyro- $\text{H}_4\text{P}_2\text{O}_7$ , and meta-phosphoric acid  $\text{HPO}_3$ . Salts of the three acids exist; the orthophosphates are the most stable and incidentally the most important\*; solutions of pyro- and meta-phosphates pass into orthophosphates slowly at the ordinary temperature, and more rapidly on boiling. Metaphosphates, unless prepared by special methods, are usually polymeric, *i.e.* are derived from  $(\text{HPO}_3)_n$ .

Orthophosphoric acid is a tribasic acid giving rise to three series of salts: primary orthophosphates, *e.g.*  $\text{NaH}_2\text{PO}_4$ ; secondary orthophosphates, *e.g.*  $\text{Na}_2\text{HPO}_4$ ; and tertiary orthophosphates, *e.g.*  $\text{Na}_3\text{PO}_4$ . If a solution of orthophosphoric acid is neutralised with sodium hydroxide solution using methyl orange as indicator, the neutral point is reached when the acid is converted into the primary phosphate (1 equivalent of alkali); with phenol phthalein as indicator, the solution will react neutral when the secondary phosphate is formed (2 equivalents of alkali); with 3 equivalents of alkali, the tertiary or normal phosphate is formed.  $\text{NaH}_2\text{PO}_4$  is neutral to methyl orange and acid to phenol phthalein,  $\text{Na}_2\text{HPO}_4$  is neutral to phenol phthalein and alkaline to methyl orange,  $\text{Na}_3\text{PO}_4$  is alkaline to most indicators because of its extended hydrolysis. Ordinary "sodium phosphate" is disodium hydrogen phosphate,  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ .

**Solubility.**—The phosphates of the alkali metals, with the exception of lithium, and of ammonium are soluble in water; the primary phosphates of the alkaline earth metals are also soluble. All the phosphates of the other metals, and also the secondary and tertiary phosphates of the alkaline earth metals, are sparingly soluble or insoluble in water.

Use disodium hydrogen phosphate,  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ .

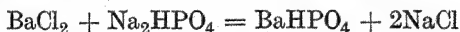
**1. Silver Nitrate Solution:** yellow precipitate of normal silver orthophosphate  $\text{Ag}_3\text{PO}_4$  (distinction from meta- and

\* These are often referred to simply as phosphates.

pyro-phosphate), soluble in dilute ammonia solution and in dilute nitric acid.

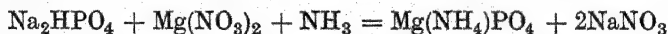


**2. Barium Chloride Solution:** white, amorphous precipitate of secondary barium phosphate  $\text{BaHPO}_4$  from neutral solutions, soluble in dilute mineral acids and in acetic acid. In the presence of dilute ammonia solution, the less soluble tertiary phosphate  $\text{Ba}_3(\text{PO}_4)_2$  is precipitated.



### 3. Magnesium Nitrate Reagent or Magnesia Mixture.

—The former is a solution containing  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{NH}_4\text{NO}_3$  and a little aqueous  $\text{NH}_3$ , and the latter is a solution containing  $\text{MgCl}_2$ ,  $\text{NH}_4\text{Cl}$  and a little aqueous  $\text{NH}_3$ : the magnesium nitrate reagent is generally preferred since it may be employed in any subsequent test with silver nitrate solution. With either reagent a white crystalline precipitate of magnesium ammonium phosphate  $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$  is produced: this precipitate is soluble in acetic acid and in mineral acids, but practically insoluble in 2.5 per cent ammonia solution (see under Magnesium, Section III, 33, reaction 5; also under Arsenic, Section III, 12, reaction 3).



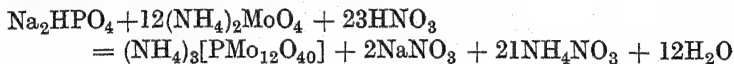
Arsenates give a similar precipitate  $\{\text{Mg}(\text{NH}_4)\text{AsO}_4 \cdot 6\text{H}_2\text{O}\}$  with either reagent. They are most simply distinguished from one another by treating the washed precipitate with silver nitrate solution containing a few drops of dilute acetic acid: the phosphate turns yellow ( $\text{Ag}_3\text{PO}_4$ ), whilst the arsenate assumes a brownish-red colour ( $\text{Ag}_3\text{AsO}_4$ ).

**4. Ammonium Molybdate Reagent.**—The addition of a large excess (2–3 ml.) of this reagent to a small volume (0.5 ml.) of a phosphate solution produces a yellow crystalline precipitate of ammonium phosphomolybdate, to which the formula  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$  was formerly assigned. The correct formula is  $(\text{NH}_4)_3[\text{PMo}_{12}\text{O}_{40}]$  or  $(\text{NH}_4)_3[\text{PO}_4(\text{Mo}_{12}\text{O}_{36})]$ . The resulting solution should be strongly acid with nitric acid; the latter is usually present in the reagent and addition is therefore unnecessary. Precipitation is accelerated by warming to a

temperature not exceeding 40°, and by the addition of ammonium nitrate solution.

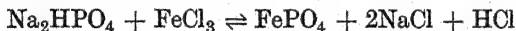
The precipitate is soluble in ammonia solution and in solutions of caustic alkalis. Large quantities of hydrochloric acid interfere with the test and should preferably be removed by evaporation to a small volume with excess of concentrated nitric acid. Reducing agents, such as sulphides, sulphites, ferrocyanides and tartrates, seriously affect the reaction, and should be destroyed before carrying out the test.

Arsenates give a similar reaction on *boiling* (see under Arsenic, Section III, 12, reaction 4). Both ammonium phosphomolybdate and ammonium arsenomolybdate dissolve on boiling with ammonium acetate solution, but only the latter yields a white precipitate on cooling.



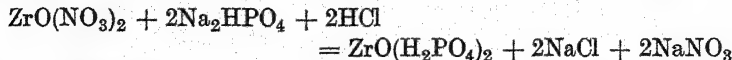
*Note.* Commercial ammonium molybdate has the formula  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  (a paramolybdate) and not  $(\text{NH}_4)_2\text{MoO}_4$ ; the latter formula is employed in the equations for purposes of simplicity, and may exist under the experimental conditions of the reaction.

**5. Ferric Chloride Solution:** yellowish-white precipitate of ferric phosphate  $\text{FePO}_4$ , soluble in dilute mineral acids, but insoluble in dilute acetic acid.



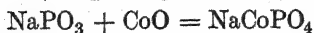
Precipitation is incomplete owing to the free mineral acid produced. If the hydrogen ions, arising from the complete ionisation of the mineral acid, are removed by the addition of the salt of a weak acid, such as ammonium or sodium acetate which give rise to the feebly dissociated acetic acid, then precipitation is almost complete. The presence of a large excess of sodium or ammonium acetate reduces the ionisation of the acetic acid still further as a result of the common ion effect (Section I, 14). This is the basis of one of the methods for the removal of phosphates, which interfere with the precipitation of Group IIIA metals, in qualitative analysis.

**6. Zirconyl Nitrate Reagent.**—When the reagent is added to a solution of a phosphate containing hydrochloric acid not exceeding *N* in concentration, a white gelatinous precipitate of zirconyl phosphate  $\text{ZrO}(\text{H}_2\text{PO}_4)_2$  or  $\text{ZrO}(\text{HPO}_4)$  is obtained. This reaction forms the basis of a simple method for the removal of phosphate prior to the precipitation of Group IIIA (compare Section VII, 7, Table II).

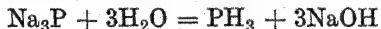
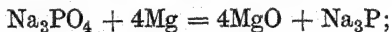


**7. Cobalt Nitrate Test.**—Phosphates when heated on charcoal and then moistened with a few drops of cobalt nitrate

solution, give a blue mass of the phosphate  $\text{NaCoPO}_4$ . This must not be confused with the blue mass produced with aluminium compounds (see Section III, 21).



**8. Magnesium.**—The only simple method for reducing the stable phosphates consists in heating with magnesium powder, whereby a phosphide is produced. The latter is readily identified by the odour and the inflammability of the phosphine formed on the addition of water. Intimately mix a small quantity of sodium phosphate with magnesium powder and heat in an ignition tube. Moisten the cold mass with water and observe the unpleasant odour of phosphine.



**†9. Ammonium Molybdate-Benzidine Test.**—In this test use is made of the fact that benzidine, which is unaffected by normal molybdates and by free molybdic acid, is oxidised in acetic acid solution by phosphomolybdic acid or by its insoluble ammonium salt (see reaction 4 above). This reaction is extremely sensitive; two coloured products are formed, *viz.* the blue reduction product of molybdenum compounds ("molybdenum blue") and the blue oxidation product of benzidine ("benzidine blue"). Moreover, solutions of phosphates which are too dilute to show a visible precipitate with the ammonium molybdate reagent will react with the molybdate reagent and benzidine to give a blue coloration.

Arsenates and silicates with ammonium molybdate yield the ammonium salts of arseno-molybdic  $\{\text{H}_3[\text{AsMo}_{12}\text{O}_{40}]\}$  and silico-molybdic  $\{\text{H}_4[\text{SiMo}_{12}\text{O}_{40}]\}$  acids respectively; these complex acids and their salts react similarly with benzidine. However, phosphates may be detected in the presence of arsenates and silicates by preventing the formation of the corresponding molybdo-acids by the use of a tartaric acid-ammonium molybdate reagent which does not react with arsenic and silicic acids but does react with phosphoric acid when the reaction is carried out on filter paper.

Hydrogen peroxide, oxalates and fluorides interfere with the precipitation of the phosphomolybdate and should therefore be absent.

Place a drop of the acid solution under test upon quantitative filter paper, add a drop of the molybdate reagent, followed by a drop of the benzidine reagent. Hold the paper over ammonia vapour. A blue stain is formed when most of the mineral acid has been neutralised.

Sensitivity: 1.25  $\mu\text{g}$ .  $\text{P}_2\text{O}_5$ . Concentration limit: 1 in 40,000.

The ammonium molybdate and the benzidine reagent are prepared as described under Silicates, Section IV, 26, reaction 7.

In the presence of silicates and/or arsenates, proceed as follows. Place a drop of the test solution upon quantitative filter paper, followed by a drop of the tartaric acid-ammonium molybdate reagent. Hold

the paper over a hot wire gauze (or over a sheet of asbestos heated on a hot plate) to accelerate the reaction. Then add a drop of the benzidine reagent and develop over ammonia vapour. A blue coloration results.

Sensitivity: 1.5  $\mu\text{g}$ .  $\text{P}_2\text{O}_5$  in the presence of 500 times the amount of  $\text{SiO}_2$ . Concentration limit: 1 in 50,000.

The tartaric acid-ammonium molybdate reagent is prepared by dissolving 15 grams of crystallised tartaric acid in 100 ml. of the ammonium molybdate reagent referred to above.

†10. **Ammonium Molybdate-Quinine Sulphate Reagent.**—Phosphates give a yellow precipitate with this reagent: the exact composition appears to be unknown.

Reducing agents (sulphides, thiosulphates, etc.) interfere since they yield "molybdenum blue"; ferrocyanides give a red coloration. Arsenates (warming is usually required), arsenites, chromates, oxalates, tartrates and silicates give a similar reaction with some variation in the colour of the precipitate. All should be removed before applying the test.

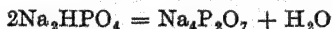
Place 1 ml. of the test solution in a semimicro test-tube and add 1 ml. of the reagent. A yellow precipitate is produced within a few minutes: gentle warming (water bath) is sometimes necessary.

Concentration limit: 1 in 20,000.

The reagent is prepared by dissolving 4.0 grams of finely powdered ammonium molybdate  $\{(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}\}$  in 20 ml. of water and adding, with stirring, a solution of 0.1 gram of quinine sulphate in 80 ml. of concentrated nitric acid.

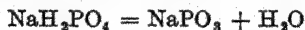
## IV, 29. REACTIONS OF PYROPHOSPHATES, $\text{P}_2\text{O}_7^{4-}$ AND OF METAPHOSPHATES, $\text{PO}_3^-$

Sodium pyrophosphate is prepared by heating disodium hydrogen phosphate:



This is the normal salt. Acid salts, e.g.  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ , are known.

Sodium metaphosphate (polymeric) may be prepared by heating microcosmic salt or sodium dihydrogen phosphate:



A number of metaphosphates are known and these may be regarded as derived from the polymeric acid  $(\text{HPO}_3)_n$ , i.e. poly-metaphosphoric acid. Calgon, used for water softening, is probably  $(\text{NaPO}_3)_6$  or  $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$ .

Pyro- and meta-phosphates give the ammonium molybdate test on warming for some time; this is doubtless due to their initial conversion in solution into orthophosphates. The chief differences between ortho-, pyro- and meta-phosphates are incorporated in the following table. The student should carry out all the tests.

## Reactions of Ortho-, Pyro- and Meta-phosphates

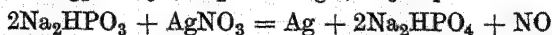
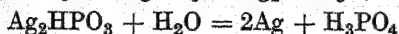
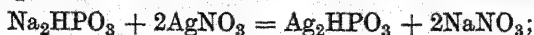
Reagent	Orthophosphate	Pyrophosphate	Metaphosphate
1. Silver nitrate solution.	Yellow ppt., soluble in dilute $\text{HNO}_3$ and in dilute $\text{NH}_3$ solution.	White ppt., soluble in dilute $\text{HNO}_3$ and in dilute $\text{NH}_3$ solution: sparingly soluble in dilute acetic acid.	White ppt. (separates slowly), soluble in dilute $\text{HNO}_3$ , in dilute $\text{NH}_3$ solution and in dilute acetic acid.
2. Albumin and dilute acetic acid.	No coagulation.	No coagulation.	Coagulation.
3. Copper sulphate solution.	Pale blue ppt.	Very pale blue ppt.	No ppt.
4. Magnesia mixture or $\text{Mg}(\text{NO}_3)_2$ reagent.	White ppt., insoluble in excess of the reagent.	White ppt., soluble in excess of reagent, but reprecipitated on boiling.	No ppt., even on boiling.
5. Cadmium chloride solution and dilute acetic acid.	No ppt.	White ppt.	No ppt.
6. Zinc sulphate solution.	White ppt., soluble in dilute acetic acid.	White ppt., insoluble in dilute acetic acid; soluble in dilute $\text{NH}_3$ solution, yielding a white ppt. on boiling.	White ppt. on warming; soluble in dilute acetic acid.

IV, 30. REACTIONS OF PHOSPHITES,  $\text{HPO}_3^{--}$ 

*Solubility.*—The phosphites of the alkali metals are soluble in water; all other metallic phosphites are insoluble in water.

Use sodium phosphite,  $\text{Na}_2\text{HPO}_3 \cdot 5\text{H}_2\text{O}$ .

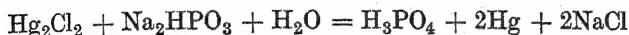
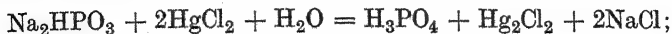
**1. Silver Nitrate Solution:** white precipitate of silver phosphite  $\text{Ag}_2\text{HPO}_3$ , which soon passes in the cold into black metallic silver. Warming is necessary with dilute solutions. Upon adding the reagent to a warm solution of a phosphite, a black precipitate of metallic silver is obtained immediately.



**2. Barium Chloride Solution:** white precipitate of barium phosphite  $\text{BaHPO}_3$ , soluble in dilute acids.

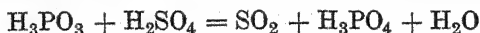


**3. Mercuric Chloride Solution:** white precipitate of calomel in the cold; on warming with excess of the phosphite solution, grey metallic mercury is produced.

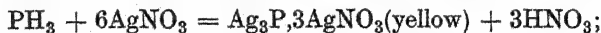
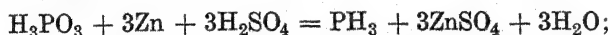


**4. Potassium Permanganate Solution:** no action in the cold with a solution acidified with acetic acid, but decolourised on warming.

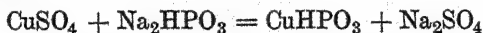
**5. Concentrated Sulphuric Acid:** no reaction in the cold with the solid salt, but on warming sulphur dioxide is evolved.



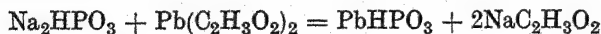
**6. Zinc and Dilute Sulphuric Acid.**—Phosphites are reduced by the nascent hydrogen to phosphine  $\text{PH}_3$ , which may be identified as described in the Gutzeit test under Arsenic (Section IV, 13); the silver nitrate paper is stained first yellow and then black.



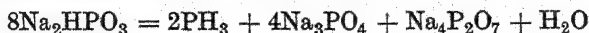
**7. Copper Sulphate Solution:** light blue precipitate of copper phosphite  $\text{CuHPO}_3$ ; the precipitate merely dissolves when it is boiled with acetic acid (compare Hypophosphites, Section IV, 31).



**8. Lead Acetate Solution:** white precipitate, insoluble in acetic acid.



**9. Action of Heat:** inflammable phosphine is evolved, and a mixture of phosphates is produced.



#### IV, 31. REACTIONS OF HYPOPHOSPHITES,

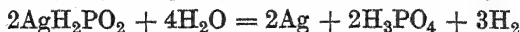
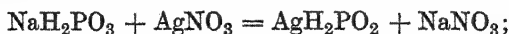


*Solubility.*—All hypophosphites are soluble in water.

Use sodium hypophosphite,  $\text{NaH}_2\text{PO}_2, \text{H}_2\text{O}$ .

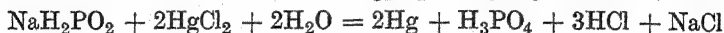
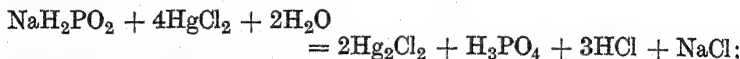
**1. Silver Nitrate Solution:** white precipitate of silver hypophosphite  $\text{AgH}_2\text{PO}_2$ , which is slowly reduced to silver at

the ordinary temperature, but more rapidly on warming, hydrogen being simultaneously evolved.

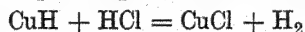
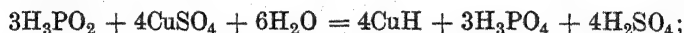


2. **Barium Chloride Solution:** no precipitate.

3. **Mercuric Chloride Solution:** white precipitate of calomel in the cold, converted by warming into grey, metallic mercury.



4. **Copper Sulphate Solution:** no precipitate in the cold, but on warming red cuprous hydride  $\text{CuH}$  is precipitated. The latter evolves hydrogen on treatment with concentrated hydrochloric acid.



5. **Potassium Permanganate Solution:** reduced immediately in the cold.

6. **Concentrated Sulphuric Acid:** reduced to sulphur dioxide (and to sulphur) by the solid salt, only on warming.

7. **Concentrated Sodium Hydroxide Solution:** hydrogen is evolved, and a phosphate is produced on warming.



8. **Zinc and Dilute Sulphuric Acid:** inflammable phosphine is evolved (see under Phosphites, Section IV, 30, reaction 6).

9. **Ammonium Molybdate Solution:** reduced to "molybdenum blue" in solution acidified with dilute sulphuric acid (difference from phosphite).

10. **Action of Heat:** phosphine is evolved, and a pyrophosphate is produced.

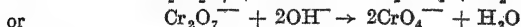
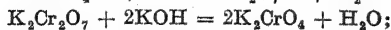
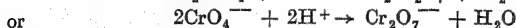
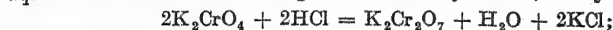


#### IV, 32. REACTIONS OF ARSENITES, $\text{AsO}_3^{---}$ AND OF ARSENATES, $\text{AsO}_4^{---}$

See under Arsenic, Sections III, 11 and III, 12.

# IV, 33. REACTIONS OF CHROMATES, $\text{CrO}_4^{--}$ (AND DICHROMATES, $\text{Cr}_2\text{O}_7^{--}$ )

The metallic chromates are usually coloured solids, yielding yellow solutions when soluble in water. In the presence of dilute mineral acids, *i.e.* of hydrogen ions, chromates are converted into dichromates; the latter yield orange-red aqueous solutions. The change is reversed by alkalis, *i.e.* by hydroxyl ions.



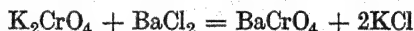
The reactions may also be expressed:



*Solubility.*—The chromates of the alkali metals and of calcium and magnesium are soluble in water; strontium chromate is sparingly soluble. Most other metallic chromates are insoluble in water. Sodium, potassium and ammonium dichromates are soluble in water.

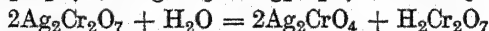
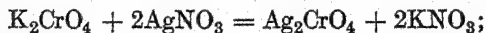
Use potassium chromate,  $\text{K}_2\text{CrO}_4$ , or potassium dichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$ .

**1. Barium Chloride Solution:** pale yellow precipitate of barium chromate  $\text{BaCrO}_4$ , insoluble in water and in acetic acid, but soluble in dilute mineral acids (for explanation, see Section I, 17).



**2. Silver Nitrate Solution:** brownish-red precipitate of silver chromate  $\text{Ag}_2\text{CrO}_4$  with a solution of a chromate. The precipitate is soluble in dilute nitric acid and in ammonia solution, but is insoluble in acetic acid. Hydrochloric acid converts the precipitate into silver chloride (white).

A reddish-brown precipitate of silver dichromate  $\text{Ag}_2\text{Cr}_2\text{O}_7$  is formed with a concentrated solution of a dichromate; this passes, on boiling with water, into the less soluble silver chromate.



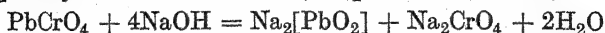
**3. Lead Acetate Solution:** yellow precipitate of lead chromate  $\text{PbCrO}_4$ , insoluble in acetic acid, but soluble in dilute nitric acid.



The precipitate is soluble in sodium hydroxide solution; acetic acid reprecipitates the chromate from the latter solution.

The solubility in sodium hydroxide solution is due to the formation of the soluble complex salt, sodium plumbite  $\text{Na}_2[\text{PbO}_2]$ , which reduces the  $\text{Pb}^{++}$  ion concentration to such an extent that the

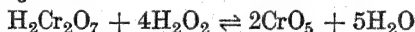
solubility product of lead chromate is no longer exceeded, and consequently the latter dissolves (compare Section I, 17).



**4. Hydrogen Peroxide.**—If an acid solution of a chromate is treated with hydrogen peroxide, a deep-blue solution of the so-called *perchromic acid* is obtained (compare Chromium, Section III, 22, reaction 6). The blue solution is very unstable and soon decomposes, yielding oxygen and a green solution of a chromic salt. The blue compound is soluble in amyl alcohol and also in amyl acetate and in diethyl ether, and can be extracted from aqueous solutions by these solvents to yield somewhat more stable solutions.

Amyl alcohol is recommended. Diethyl ether is not recommended for general student use owing to its highly inflammable character and also because it frequently contains peroxides after storage for comparatively short periods: a blank test is therefore necessary. Peroxides may be removed from diethyl ether by shaking with a concentrated solution of a ferrous salt or with sodium sulphite.

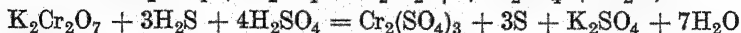
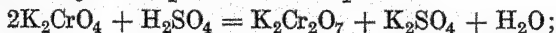
The blue coloration is attributed to the presence of chromic diperoxide  $\text{CrO}_5$ :



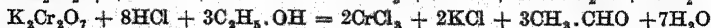
The enhanced stability in solutions of amyl alcohol, ether, etc., is due to the formation of complexes with these oxygen-containing compounds.

Just acidify a cold solution of a chromate with dilute sulphuric acid or dilute nitric acid, add 1–2 ml. of amyl alcohol, then 1 ml. of 10-volume (3 per cent) hydrogen peroxide solution dropwise and with shaking after each addition: the organic layer is coloured blue. The chromic peroxide is more stable below  $0^\circ\text{C}$  than at the laboratory temperature.

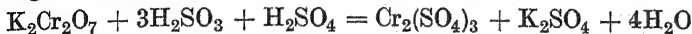
**5. Hydrogen Sulphide.**—An acid solution of a chromate is reduced by this reagent to a green solution of a chromic salt, accompanied by the separation of sulphur.\*



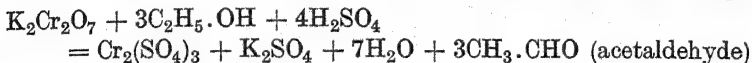
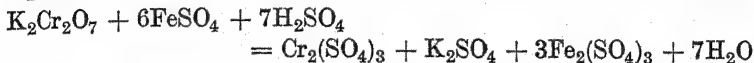
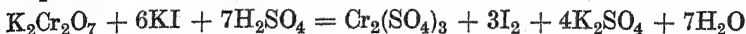
\* In qualitative analysis, the production of sulphur in the reduction of dichromates by hydrogen sulphide is sometimes troublesome. This can be avoided (a) by heating the solid substance with concentrated hydrochloric acid, evaporating off most of the acid and then diluting with water, or (b) by warming with hydrochloric acid and alcohol or 10 per cent formaldehyde solution. The use of sulphur dioxide is not recommended as sulphuric acid is formed, and this will precipitate lead, strontium and barium, if these metals are present.



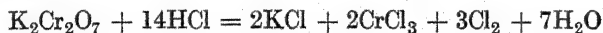
6. **Sulphur Dioxide:** in the presence of dilute mineral acid, a green chromic salt is produced.



Chromates in acid solution, or dichromates, are similarly reduced to green chromic salts by potassium iodide, ferrous sulphate and ethyl alcohol.



7. **Concentrated Hydrochloric Acid.**—On heating a solid chromate or dichromate with concentrated hydrochloric acid, chlorine is evolved, and a solution of chromic chloride is produced.



8. **Concentrated Sulphuric Acid and a Chloride.**—See chromyl chloride test under Chlorides, Section IV, 14, reaction 5; also Section IV, 45, 5.

9. **Diphenylcarbazide Reagent.**—The solution is acidified with dilute sulphuric acid or with dilute acetic acid, and 1–2 ml. of the reagent added. A deep red coloration is produced. With small quantities of chromates, the solution is coloured violet.

Full details of the use of the reagent as a spot test are given under Chromium, Section III, 22, reaction 7.

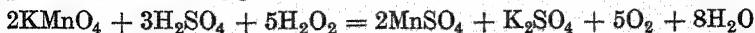
10. **Chromotropic Acid Test.**—A red coloration, best seen by transmitted light, is given by chromates. For details, see under Chromium, Section III, 22, reaction 8.

#### IV, 34. REACTIONS OF PERMANGANATES $\text{MnO}_4^-$

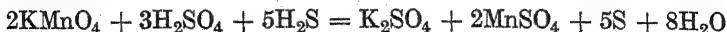
*Solubility.*—All permanganates are soluble in water forming purple (reddish-violet) solutions.

Use potassium permanganate,  $\text{KMnO}_4$ .

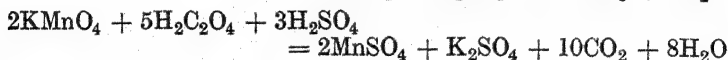
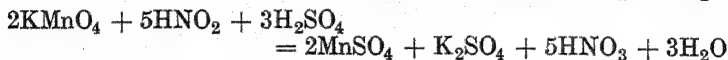
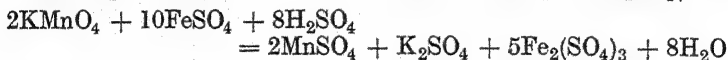
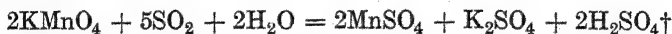
1. **Hydrogen Peroxide.**—The addition of this reagent to a solution of potassium permanganate, acidified with dilute sulphuric acid, results in decolourisation and the evolution of pure but moist oxygen.



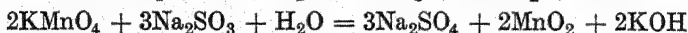
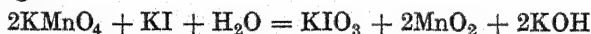
**2. Hydrogen Sulphide:** in the presence of dilute sulphuric acid, the purple colour of the solution is discharged and sulphur is precipitated.\*



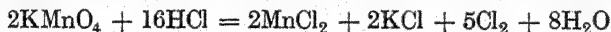
Similar results are obtained with other reducing agents in the presence of dilute sulphuric acid. These include sulphur dioxide, ferrous sulphate, potassium iodide, sodium nitrite and oxalic acid; in the last case, the reaction proceeds best at about 60°.



In *alkaline* solution, the permanganate is decolourised, but manganese dioxide is precipitated. In the presence of sodium hydroxide solution, potassium iodide is converted into potassium iodate, and sodium sulphite solution into sodium sulphate on boiling.



**3. Concentrated Hydrochloric Acid.**—All permanganates on boiling with concentrated hydrochloric acid evolve chlorine.

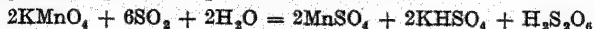


**4. Concentrated Sulphuric Acid (GREAT DANGER).**—Permanganates dissolve in this reagent to yield a green solution, which contains manganese heptoxide (permanganic anhydride)  $\text{Mn}_2\text{O}_7$ ; the solution is liable to explode spontaneously at the

\* To avoid the production of sulphur by the reduction of potassium permanganate by hydrogen sulphide in systematic qualitative analysis, the solution may be reduced with formaldehyde solution, or the solid substance may be boiled with concentrated hydrochloric acid. The use of sulphur dioxide is not recommended (see footnote in connexion with Chromates, Section IV, 33, reaction 5).

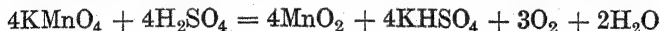
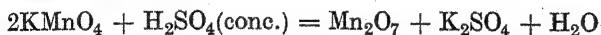


† Some dithionic acid  $\text{H}_2\text{S}_2\text{O}_6$  may be formed in this reaction, the quantity being dependent upon the experimental conditions.

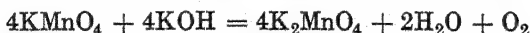


ordinary temperature, and a very vigorous explosion may result on warming. The student is therefore warned not to carry out this experiment except with minute quantities of materials (not more than 0.05 gram) and in the latter case under the direct supervision of the teacher. The experiment is best omitted.

Upon warming potassium permanganate with *dilute* sulphuric acid, oxygen is evolved.



**5. Potassium Hydroxide Solution.**—Upon warming a concentrated solution of potassium permanganate with concentrated potassium hydroxide solution, a green solution of potassium manganate is produced and oxygen is evolved. When the manganate solution is poured into a large volume of water or is acidified with dilute sulphuric acid, the purple colour of the potassium permanganate is restored.



A manganate is produced when a manganese compound is fused with potassium nitrate and sodium carbonate (see Section III, 26).

**6. Action of Heat.**—When potassium permanganate is heated in a test-tube, pure oxygen is evolved, and a black residue of potassium manganate  $\text{K}_2\text{MnO}_4$  and manganese dioxide remains behind. Upon extracting with a little water and filtering, a green solution of potassium manganate is obtained.



#### IV, 35. REACTIONS OF ACETATES, $\text{C}_2\text{H}_3\text{O}_2^-$

**Solubility.**—All normal acetates, with the exception of silver and mercurous acetates which are sparingly soluble, are readily soluble in water. Some basic acetates, *e.g.* those of iron, aluminium and chromium, are insoluble in water. The free acid,  $\text{CH}_3\cdot\text{CO}_2\text{H}$  or  $\text{H}\cdot\text{C}_2\text{H}_3\text{O}_2$ , is a colourless liquid with a pungent odour, boiling point  $117^\circ$ , melting point  $17^\circ$  and is miscible with water in all proportions; it has a corrosive action on the skin.

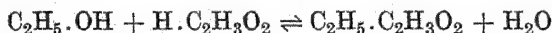
Use sodium acetate,  $\text{Na}\cdot\text{C}_2\text{H}_3\text{O}_2\cdot 3\text{H}_2\text{O}$  (or  $\text{CH}_3\cdot\text{CO}_2\text{Na}\cdot 3\text{H}_2\text{O}$ ).

**1. Dilute Sulphuric Acid:** acetic acid, easily recognised by its vinegar-like odour, is evolved on warming.



**2. Concentrated Sulphuric Acid:** acetic acid is evolved on heating, together with sulphur dioxide, the latter tending to mask the penetrating odour of the concentrated acetic acid vapour. The test with dilute sulphuric acid, in which the acetic acid vapour is diluted with steam, is therefore to be preferred as a test for an acetate.

**3. Ethyl Alcohol and Concentrated Sulphuric Acid.**—One gram of the solid acetate is treated with 1 ml. of concentrated sulphuric acid and 2–3 ml. of rectified spirit in a test-tube, and the whole gently warmed for several minutes; ethyl acetate  $C_2H_5.C_2H_3O_2$  is formed, which is recognised by its pleasant, fruity odour. On cooling and dilution with water on a clock glass, the fragrant odour will be more readily detected.



(the sulphuric acid acts as a dehydrating agent).

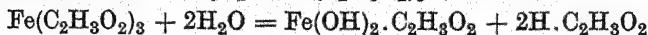
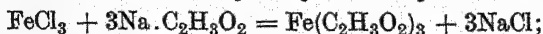
It is preferable to use *iso*-amyl alcohol because the odour of the resulting *iso*-amyl acetate is more readily distinguished from the alcohol itself than is the case with ethyl alcohol. It is well to run a parallel test with a known acetate and to compare the odours of the two products.

**4. Silver Nitrate Solution:** a white, crystalline precipitate of silver acetate  $Ag.C_2H_3O_2$  is produced in concentrated solutions in the cold. The precipitate is more soluble in boiling water (10.4 grams per litre at 20° and 25.2 grams per litre at 80°) and readily soluble in dilute ammonia solution.



**5. Barium, Calcium or Mercuric Chloride Solution:** no precipitate.

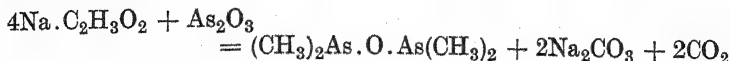
**6. Ferric Chloride Solution:** deep-red coloration, due to ferric acetate  $Fe(C_2H_3O_2)_3$ , is produced with practically neutral solutions of acetates. On diluting and boiling the red solution, the iron is precipitated as basic ferric acetate  $Fe(OH)_2.C_2H_3O_2$ . The coloration is destroyed by dilute hydrochloric acid.



**7. Cacodyl Oxide Reaction.**—If a dry acetate, preferably that of sodium or potassium, is heated in an ignition tube or test-tube with a small quantity of arsenious oxide, an extremely nauseating odour of cacodyl oxide is produced. All cacodyl compounds are *extremely* poisonous; the experiment must



therefore be performed on a very small scale, and preferably in the fume chamber. Mix not more than 0.2 gram of sodium acetate with 0.2 gram of arsenious oxide in an ignition tube and warm; observe the extremely unpleasant odour that is produced.



**8. Lanthanum Nitrate Test.**—Treat 0.5 ml. of the acetate solution with 0.5 ml. of a 5 per cent lanthanum nitrate solution, add 0.5 ml. of iodine solution and a few drops of dilute ammonia solution, and heat slowly to the boiling point. A blue colour is produced; this is probably due to the adsorption of the iodine by the basic lanthanum acetate. This reaction provides an extremely sensitive test for an acetate.

Sulphates and phosphates interfere, but can be removed by precipitation with barium nitrate solution before applying the test. Propionates give a similar reaction.

† The spot-test technique is as follows. Mix a drop of the test solution on a spot plate with a drop of 5 per cent lanthanum nitrate solution and a drop of 0.01*N* iodine. Add a drop of *N* ammonia solution. Within a few minutes a blue to blue-brown ring will develop round the drop of ammonia solution.

Sensitivity: 50  $\mu\text{g}$ .  $\text{H} \cdot \text{C}_2\text{H}_3\text{O}_2$ . Concentration limit: 1 in 2,000.

†9. **Formation of Indigo Test.**—The test depends upon the conversion of acetone, formed by the dry distillation of acetates (see reaction 10), into indigo. No other fatty acids give this test, but the sensitivity is reduced in their presence.

Mix the solid test sample with calcium carbonate or, alternatively, evaporate a drop of the test solution to dryness with calcium carbonate; both operations may be carried out in the hard glass tube of Fig. II, 6, 15. Cover the open end of the tube with a strip of quantitative filter paper moistened with a freshly prepared solution of *o*-nitrobenzaldehyde in 2*N* sodium hydroxide, and hold the paper in position with a small glass cap or a small watch glass. Insert the tube into a hole in an asbestos or "uralite" sheet and heat the tube gently. Acetone is evolved which colours the paper blue or bluish-green. For minute amounts of acetates, it is best to remove the filter paper after the reaction and treat it with a drop of dilute hydrochloric acid; the original yellow colour of the paper is thus bleached and the blue colour of the indigo is more readily apparent.

Sensitivity: 60  $\mu\text{g}$ .  $\text{H} \cdot \text{C}_2\text{H}_3\text{O}_2$

**10. Action of Heat.**—All acetates decompose upon strong ignition, yielding the highly inflammable acetone  $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3$  and a residue, which consists of the carbonates for the alkali acetates, of the oxides for the acetates of the alkaline earth and heavy metals, and of the metal for the acetates of silver

and the noble metals. Carry out the experiment in an ignition tube with sodium acetate and lead acetate.

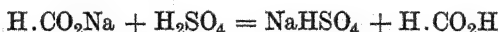


#### IV, 36. REACTIONS OF FORMATES, $\text{H} \cdot \text{CO}_2^-$

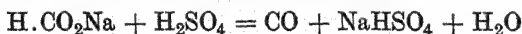
*Solubility.*—With the exception of the lead, silver and mercurous salts which are sparingly soluble, most formates are soluble in water. The free acid  $\text{H} \cdot \text{CO}_2\text{H}$  is a pungent smelling liquid, boiling point  $100.5^\circ$ , melting point  $8^\circ$ , miscible with water in all proportions, and producing blisters when allowed to come into contact with the skin.

Use sodium formate,  $\text{H} \cdot \text{CO}_2\text{Na}$ .

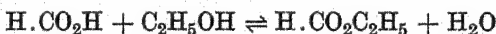
**1. Dilute Sulphuric Acid:** formic acid is liberated, the pungent odour of which can be detected on warming the mixture.



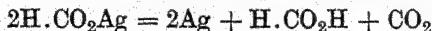
**2. Concentrated Sulphuric Acid:** carbon monoxide (*highly poisonous*) is evolved on warming; the gas should be ignited and the characteristic blue flame obtained.



**3. Ethyl Alcohol and Concentrated Sulphuric Acid:** a pleasant odour, due to ethyl formate  $\text{H} \cdot \text{CO}_2\text{C}_2\text{H}_5$ , is apparent on warming (for details, see under Acetates, Section IV, 35, reaction 3).

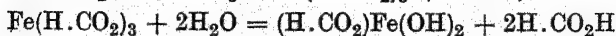
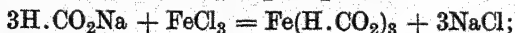


**4. Silver Nitrate Solution:** white precipitate of silver formate  $\text{H} \cdot \text{CO}_2\text{Ag}$  in neutral solutions, slowly reduced at the ordinary temperature and more rapidly on warming, a black precipitate of silver being formed (distinction from acetate). With very dilute solutions, the silver may be deposited in the form of a mirror on the walls of the tube.

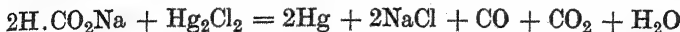
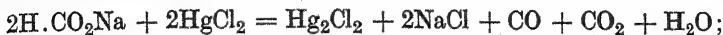


**5. Barium or Calcium Chloride Solution:** no precipitate.

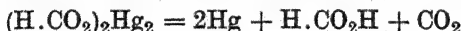
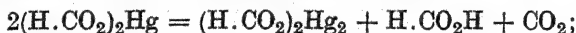
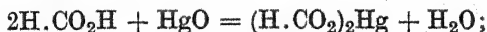
**6. Ferric Chloride Solution:** a red coloration, due to ferric formate  $\text{Fe}(\text{H} \cdot \text{CO}_2)_3$ , is produced in practically neutral solutions; the colour is discharged by hydrochloric acid. If the red solution is diluted and boiled, a brown basic ferric formate  $(\text{H} \cdot \text{CO}_2)\text{Fe}(\text{OH})_2$  is precipitated.



7. **Mercuric Chloride Solution:** white precipitate of mercurous chloride  $\text{Hg}_2\text{Cl}_2$  is produced on warming; this passes into grey, metallic mercury in presence of excess of the formate solution (distinction from acetate).



8. **Mercuric Formate Test.**—Free formic acid is necessary for this test. The solution of the formate is acidified with dilute sulphuric acid and shaken vigorously with a little mercuric oxide; it is then filtered from the undissolved oxide. The filtrate, which contains mercuric formate  $(\text{H}.\text{CO}_2)_2\text{Hg}$ , on boiling gives momentarily a white precipitate of mercurous formate  $(\text{H}.\text{CO}_2)_2\text{Hg}_2$ , which rapidly changes to a grey precipitate of metallic mercury.

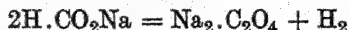


†9. **Formaldehyde-Chromotropic Acid Test.**—Formic acid  $\text{H}.\text{COOH}$  is reduced to formaldehyde  $\text{H}.\text{CHO}$  by magnesium and hydrochloric acid. The formaldehyde is identified by its reaction with chromotropic acid (see Section III, 22, reaction 8) in strong sulphuric acid when a violet-pink coloration appears. Other aliphatic aldehydes do not give the violet coloration.

Place a drop or two of the test solution in a semimicro test-tube, add a drop or two of dilute hydrochloric acid, followed by magnesium powder until the evolution of gas ceases. Introduce 3 ml. of sulphuric acid (3 acid : 2 water) and a little solid chromotropic acid, and warm to  $60^\circ\text{C}$ . A violet-pink coloration appears within a few minutes.

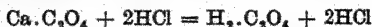
Sensitivity: 1.5  $\mu\text{g}$ .  $\text{H}.\text{COOH}$ . Concentration limit: 1 in 20,000.

10. **Action of Heat.**—Cautious ignition of the formates of the alkali metals yields the corresponding oxalates (for tests, see Section IV, 37) and hydrogen.



#### IV, 37. REACTIONS OF OXALATES, $\text{C}_2\text{O}_4^{--}$

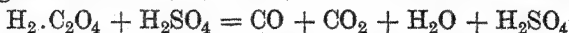
**Solubility.**—The oxalates of the alkali metals and of ferrous iron are soluble in water; all other oxalates are either insoluble or sparingly soluble in water. They are all soluble in dilute acids:



Some of the oxalates dissolve in a concentrated solution of oxalic acid by virtue of the formation of soluble acid or complex oxalates. Oxalic acid (a dibasic acid) is a colourless, crystalline solid  $\text{H}_2\text{C}_2\text{O}_4.2\text{H}_2\text{O}$  (or  $\text{HO}_2\text{C}.\text{CO}_2\text{H}.2\text{H}_2\text{O}$ ), and becomes anhydrous on heating to  $110^\circ$ ; it is readily soluble in water (111 grams per litre at  $20^\circ$ ).

Use sodium oxalate,  $\text{Na}_2\text{C}_2\text{O}_4$ , or ammonium oxalate,  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ .

**1. Concentrated Sulphuric Acid:** decomposition of all solid oxalates occurs with the evolution of carbon monoxide and carbon dioxide; the latter can be detected by passing the escaping gases through lime water (distinction from formate) and the former by burning it at the mouth of the tube. With dilute sulphuric acid, there is no visible action; in the presence of manganese dioxide, however, carbon dioxide is evolved.



(the sulphuric acid acts as a dehydrating agent).

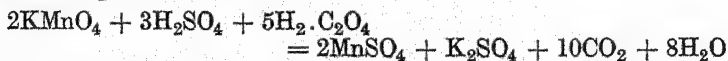
**2. Silver Nitrate Solution:** white, curdy precipitate of silver oxalate  $\text{Ag}_2\text{C}_2\text{O}_4$ , sparingly soluble in water, soluble in ammonia solution and in dilute nitric acid.



**3. Calcium Chloride Solution:** white, crystalline precipitate of calcium oxalate  $\text{CaC}_2\text{O}_4$  from neutral solutions, insoluble in dilute acetic acid, oxalic acid and in ammonium oxalate solution, but soluble in dilute hydrochloric acid and in dilute nitric acid. It is the most insoluble of all oxalates (0.0067 gram per litre at  $13^\circ$ ) and is even precipitated by calcium sulphate solution and acetic acid. Barium chloride solution similarly gives a white precipitate of barium oxalate  $\text{BaC}_2\text{O}_4$ , sparingly soluble in water (0.016 gram per litre at  $8^\circ$ ), but soluble in solutions of acetic and of oxalic acids.



**4. Potassium Permanganate Solution:** decolourised when warmed in acid solution to  $60^\circ$ – $70^\circ$ . The bleaching of permanganate solution is also effected by many other organic compounds, but if the evolved carbon dioxide is tested for by the lime water reaction (Section IV, 2, reaction 1), the test becomes specific for oxalates.



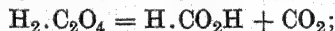
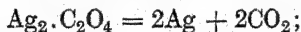
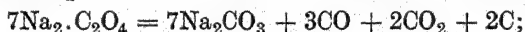
**5. Resorcinol Test.**—Place a few drops of the test solution in a test-tube: add several drops of dilute sulphuric acid and a speck or two of magnesium powder. When the metal has dissolved, add about 0.1 gram of resorcinol, and shake until dissolved. Cool. Carefully pour down the side of the tube 3–4 ml. of concentrated sulphuric acid. A blue ring will form at the junction of the two liquids. Upon warming the sulphuric acid layer at the bottom of the tube very gently

(CAUTION), the blue colour spreads downwards from the interface and eventually colours the whole of the sulphuric acid layer.

Citrates do not interfere. In the presence of tartrates, a blue ring is obtained in the cold or upon very gentle warming (compare similar test under Tartrates in the following Section).

**6. Manganous Sulphate Test.**—A solution of manganous sulphate is treated with sodium hydroxide solution, and the resulting mixture warmed gently to convert it into manganomanganic hydroxide. After cooling, the solution of the oxalate, made acid with dilute sulphuric acid, is added. The precipitate dissolves and a red colour is produced. The latter is probably due to the formation of the complex ion  $[\text{Mn}(\text{C}_2\text{O}_4)_3]^{---}$ .

**7. Action of Heat.**—All oxalates decompose upon ignition. Those of the alkali metals and of the alkaline earths yield chiefly the carbonates and carbon monoxide; a little carbon is also formed. The oxides of the metals whose carbonates are easily decomposed into stable oxides, are converted into carbon monoxide, carbon dioxide and the oxide, *e.g.* magnesium and zinc oxalates. Silver oxalate yields silver and carbon dioxide; silver oxide decomposes on heating. Oxalic acid decomposes into carbon dioxide and formic acid, the latter being further partially decomposed into carbon monoxide and water.



†**8. Formation of Aniline Blue Test.**—Upon heating insoluble oxalates with syrupy phosphoric acid and diphenylamine or upon heating together oxalic acid and diphenylamine, the dyestuff aniline blue (or diphenylamine blue) is formed. Formates, acetates, tartrates, citrates, succinates, benzoates and salts of other organic acids do not react under these experimental conditions. In the presence of other anions which are precipitated by calcium chloride solution, *e.g.* tartrate, sulphate, sulphite, phosphate and fluoride, it is best to heat the precipitate formed by calcium chloride with phosphoric acid as detailed below.

Place a few milligrams of the test sample (or, alternatively, use the residue obtained by evaporating 2 drops of the test solution to dryness) in a micro test-tube, add a little pure diphenylamine and melt over a free flame. When cold, take up the melt in a drop or two of alcohol when the latter will be coloured blue.

Sensitivity: 5  $\mu\text{g}$ .  $\text{H}_2\text{C}_2\text{O}_4$ . Concentration limit: 1 in 10,000

In the presence of anions which are precipitated by calcium chloride solution, proceed as follows. Precipitate the acetic acid test solution with calcium chloride solution, and collect the precipitate on a filter or in a centrifuge tube. Remove the water from the precipitate either by drying or by washing with alcohol and ether. Mix a small amount of the precipitate with diphenylamine in a dry micro test-tube, add a little syrupy phosphoric acid, and heat gently over a free flame. Calcium phosphate and free oxalic acid are formed, and the latter condenses with the diphenylamine to aniline blue and colours the hot phosphoric acid blue. The colour disappears on cooling. Dissolve the melt in alcohol, when a blue coloration appears. Pour the alcoholic solution into water thus precipitating the excess of diphenylamine, which is coloured light blue by the adsorption of the dyestuff. The dye may be extracted from aqueous solution by ether.

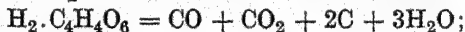
#### IV, 38. REACTIONS OF TARTRATES, $C_4H_4O_6^{--}$

**Solubility.**—Tartaric acid,  $HO_2C.CH(OH).CH(OH).CO_2H$  or  $H_2.C_4H_4O_6$ , is a crystalline solid, which is extremely soluble in water; it is a dibasic acid. The potassium and ammonium acid salts are sparingly soluble in water; those of the other alkali metals are readily soluble. The normal tartrates of the alkali metals are easily soluble, those of the other metals being sparingly soluble in water, but dissolve in solutions of alkali tartrates forming complex salts, which often do not give the typical reactions of the metals present.

The most important commercial salts are "tartar emetic"  $K(SbO).C_4H_4O_6.0.5H_2O$ , "Rochelle salt"  $KNa.C_4H_4O_6.4H_2O$  and "cream of tartar"  $KH.C_4H_4O_6$ .

Use Rochelle salt,  $KNa.C_4H_4O_6.4H_2O$ .

**1. Concentrated Sulphuric Acid.**—When a solid tartrate is heated with concentrated sulphuric acid, it is decomposed in a complex manner. *Charring* occurs almost immediately (owing to the separation of carbon), carbon dioxide and carbon monoxide are evolved, together with some sulphur dioxide; the last-named probably arises from the reduction of the sulphuric acid by the carbon. An empyreumatic odour, reminiscent of burnt sugar, can be detected in the evolved gases. Dilute sulphuric acid has no visible action.



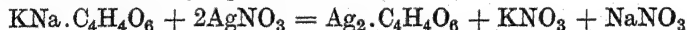
**2. Silver Nitrate Solution:** white, curdy precipitate of silver tartrate  $Ag_2.C_4H_4O_6$  from neutral solutions of tartrates, soluble in excess of the tartrate solution, in dilute ammonia solution and in dilute nitric acid. On warming the ammoniacal solution, metallic silver is precipitated; this can be deposited in the form of a mirror under suitable conditions.

The silver mirror test is best performed as follows. The solution of the tartrate is acidified with dilute nitric acid, excess of silver nitrate solution added and any precipitate present filtered off. Very dilute ammonia solution (approx-

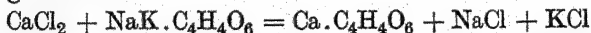
mately  $M/50$ ) is then added to the solution until the precipitate at first formed is *nearly* redissolved, the solution is filtered, and the filtrate collected in a clean test-tube; the latter is then placed in a beaker of boiling water. A brilliant mirror is formed on the sides of the tube after a few minutes. The test-tube may be cleaned either by boiling with chromic acid mixture or by boiling it with a little sodium hydroxide solution, and then rinsing it well with distilled water.

An *alternative method* for carrying out the silver mirror test is the following. Prepare ammoniacal silver nitrate solution by placing 5 ml. of silver nitrate solution in a thoroughly clean test-tube and add 2–3 drops of dilute sodium hydroxide solution; add dilute ammonia solution dropwise until the precipitated silver oxide is *almost* redissolved (this procedure reduces the danger of the formation of the explosive silver azide  $\text{AgN}_3$  to a minimum). Introduce about 0.5 ml. of the neutral tartrate solution. Place the tube in warm water. A silver mirror is formed in a few minutes.

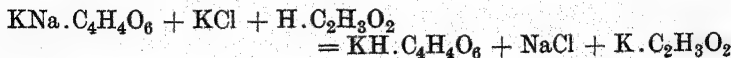
The reaction is interfered with by other acids. It is best to isolate the potassium hydrogen tartrate, as in reaction 4 below, before carrying out the test.



**3. Calcium Chloride Solution:** white, crystalline precipitate of calcium tartrate  $\text{Ca} \cdot \text{C}_4\text{H}_4\text{O}_6$  with a concentrated neutral solution. The precipitate is soluble in dilute acetic acid (difference from oxalate), in dilute mineral acids and in cold alkali solutions. An excess of the reagent must be added because calcium tartrate dissolves in an excess of an alkali tartrate solution forming a complex tartrate ion,  $[\text{Ca}(\text{C}_4\text{H}_4\text{O}_6)_2]^-$ . Precipitation is slow in dilute solutions, but may be accelerated by vigorous shaking or by rubbing the walls of the test-tube with a glass rod.



**4. Potassium Chloride Solution.**—When a concentrated, neutral solution of a tartrate is treated with a solution of a potassium salt (*e.g.* potassium chloride or potassium acetate) and then acidified with acetic acid, a colourless crystalline precipitate of potassium hydrogen tartrate  $\text{KH} \cdot \text{C}_4\text{H}_4\text{O}_6$  is obtained. The precipitate forms slowly in dilute solutions; crystallisation is induced by vigorous shaking or by rubbing the walls of the vessel with a glass rod.



**5. Fenton's Test.**—Add 1 drop of a saturated solution of ferrous sulphate to about 5 ml. of the neutral or acid solution of the tartrate, and then 2–3 drops of hydrogen peroxide solution (10 volume). A deep violet or blue coloration is developed on adding excess of sodium hydroxide solution. The colour becomes more intense upon the addition of a drop of ferric chloride solution.

The violet colour is due to the formation of a salt of dihydroxy-maleic acid  $\text{CO}_2\text{H}.\text{C}(\text{OH}) = \text{C}(\text{OH}).\text{CO}_2\text{H}$ .

The test is not given by citrates, malates or succinates.

**6. Resorcinol Test.**—Place a few drops of the test solution in a test-tube; add several drops of dilute sulphuric acid and a speck or two of magnesium powder. When the metal has dissolved, add about 0.1 gram of resorcinol, and shake until dissolved. Cool. Carefully pour down the side of the tube 3–4 ml. of concentrated sulphuric acid. Upon warming the sulphuric acid layer at the bottom of the tube very gently (*CAUTION*), a red layer (or ring) forms at the junction of the two liquids. With continued *gentle* heating, the red colour spreads downwards from the interface and eventually colours the whole of the sulphuric acid layer.

Citrates do not interfere. In the presence of oxalate, a blue ring is formed in the cold and on *gentle* warming of the sulphuric acid layer at the bottom of the tube the blue coloration spreads downwards into the concentrated acid layer and a red ring forms at the interface.

The colour is due to the formation of a condensation product of resorcinol  $\text{C}_6\text{H}_4(\text{OH})_2$  and glycollic aldehyde  $\text{CH}_2\text{OH}.\text{CHO}$ , the latter arising from the action of the sulphuric acid upon the tartaric acid. The formula of the condensation product is  $\text{CH}_2\text{OH}.\text{CH}[\text{C}_6\text{H}_3(\text{OH})_2]_2$ .

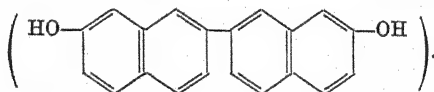
**7. Copper Hydroxide Test.**—Tartrates dissolve copper hydroxide in the presence of excess of alkali hydroxide solution to form the dark blue cupri-tartrate ion, which is best detected by filtering the solution. If only small quantities of tartrate are present, the filtrate should be acidified with acetic acid and tested for copper by the potassium ferrocyanide test. Arsenites, ammonium salts and organic compounds convertible into tartaric acid also give a blue coloration, and should therefore be absent or be removed.

The experimental details are as follows. Treat the test solution with an equal volume of 2*N* sodium or potassium hydroxide (or treat the test solid directly with a few ml. of the alkali hydroxide solution, warm for a few minutes with stirring and then cool), add a few drops of *M* copper sulphate solution



(i.e. just sufficient to yield a visible precipitate of cupric hydroxide), shake the mixture vigorously for 5 minutes, and filter. If the filtrate is not clear, warm to coagulate the colloidal copper hydroxide and filter again. A distinct blue coloration indicates the presence of a tartrate. If a pale coloration is obtained, it is advisable to add concentrated ammonia solution dropwise when the blue colour intensifies; it is perhaps better to acidify with 2*N* acetic acid and add potassium ferrocyanide solution to the clear solution where-upon a reddish-brown precipitate or (with a trace of a tartrate) a red coloration is obtained.

#### †8. $\beta\beta$ -Dinaphthol Test



When a solution of  $\beta\beta'$ -dinaphthol in concentrated sulphuric acid is heated with tartaric acid, a green coloration is obtained. Oxalic, citric, succinic and cinnamic acids do not interfere.

Heat a few milligrams of the solid test sample or a drop of the test solution with 1-2 ml. of the dinaphthol reagent in a water bath at 85°C for 30 minutes. A luminous green fluorescence appears during the heating, which intensifies on cooling, and at the same time the violet fluorescence of the reagent disappears.

Sensitivity: 10  $\mu$ g. tartaric acid. Concentration limit: 1 in 5,000.

The reagent consists of a solution of 0.05 gram of  $\beta\beta'$ -dinaphthol in 100 ml. of concentrated sulphuric acid.

**9. Action of Heat.**—The tartrates and also tartaric acid decompose in a complex manner on heating; charring takes place, a smell of burnt sugar is apparent and inflammable vapours are evolved.

### IV, 39. REACTIONS OF CITRATES, $C_6H_5O_7$ ---

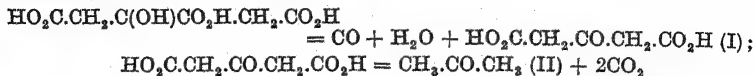
**Solubility.**—Citric acid,  $HO_2C \cdot CH_2 \cdot C(OH)CO_2H \cdot CH_2 \cdot CO_2H$ ,  $H_2O$  or  $H_3 \cdot C_6H_5O_7 \cdot H_2O$ , is a crystalline solid which is very soluble in water; it becomes anhydrous at 55° and melts at 160°. It is a tribasic acid, and therefore gives rise to three series of salts. The normal citrates of the alkali metals dissolve readily in water; other metallic citrates are sparingly soluble. The acid citrates are more soluble than the acid tartrates.

Use sodium citrate,  $Na_3 \cdot C_6H_5O_7 \cdot 2H_2O$ .

**1. Concentrated Sulphuric Acid.**—When a solid citrate is heated with concentrated sulphuric acid, carbon monoxide and carbon dioxide are evolved; the solution *slowly* darkens owing to the separation of carbon, and sulphur dioxide is

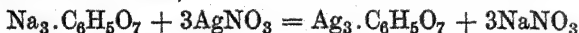
evolved (compare Tartrates, Section IV, 30, which char almost immediately).

The first products of the reaction are carbon monoxide and acetone dicarboxylic acid (I); the latter undergoes further partial decomposition into acetone (II) and carbon dioxide.

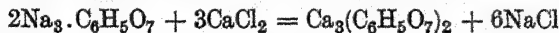


Use may be made of the intermediate formation of acetone dicarboxylic acid and of the interaction of the latter with sodium nitroprusside solution to yield a red coloration as a test for citrates. When about 0.5 grams of a citrate or of citric acid is treated with 1 ml. of concentrated sulphuric acid for 1 minute, the mixture cooled, cautiously diluted with water, rendered alkaline with sodium hydroxide solution and then a few c.c. of a freshly prepared solution of sodium nitroprusside added, an intense red coloration results.

**2. Silver Nitrate Solution:** white, curdy precipitate of silver citrate  $\text{Ag}_3 \cdot \text{C}_6\text{H}_5\text{O}_7$  from neutral solutions. The precipitate is soluble in dilute ammonia solution, and this solution undergoes only very slight reduction to silver on boiling (distinction from tartrate).



**3. Calcium Chloride Solution:** no precipitate with neutral solutions in the cold (difference from tartrate), but on boiling for several minutes a crystalline precipitate of calcium citrate  $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 4\text{H}_2\text{O}$  is produced. If sodium hydroxide solution is added to the cold solution containing excess of calcium chloride, there results an immediate precipitation of amorphous calcium citrate, insoluble in solutions of caustic alkalis, but soluble in ammonium chloride solution; on boiling the ammonium chloride solution, crystalline calcium citrate is precipitated, which is now insoluble in ammonium chloride solution.



**4. Cadmium Chloride Solution:** white, gelatinous precipitate of cadmium citrate  $\text{Cd}_3(\text{C}_6\text{H}_5\text{O}_7)_2$ , practically insoluble in boiling water, but readily soluble in warm acetic acid (tartrate gives no precipitate).



**5. Denigès' Test.**—Add 0.5 ml. of acid mercuric sulphate solution to 3 ml. of the citrate solution, heat to boiling and then add a few drops of a 2 per cent solution of potassium permanganate. Decolourisation of the permanganate will take place rapidly and then, somewhat suddenly, a heavy white precipitate, consisting of the double salt of basic mercuric sulphate with mercuric acetone dicarboxylate

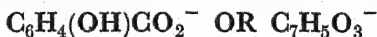


is formed. Salts of the halogen acids interfere and must therefore be removed before carrying out the test.

The **reagent** (an acid solution of mercuric sulphate) is prepared by adding 10 ml. of concentrated sulphuric acid slowly to 50 ml. of water, and dissolving 2.5 grams of mercuric oxide in the hot solution.

**6. Action of Heat.**—Citrates and citric acid char on heating; carbon monoxide, carbon dioxide and acrid-smelling vapours are evolved.

#### IV, 40. REACTIONS OF SALICYLATES,

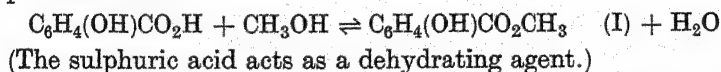


**Solubility.**—Salicylic acid  $\text{C}_6\text{H}_4(\text{OH})\text{CO}_2\text{H}$  (*o*-hydroxybenzoic acid) forms colourless needles, which melt at  $155^\circ$ . The acid is sparingly soluble in cold water, but more soluble in hot water, from which it can be recrystallised. It is readily soluble in alcohol and ether. With the exception of the lead, mercury, silver and barium salts, the monobasic salts  $\text{C}_6\text{H}_4(\text{OH})\text{CO}_2\text{M}$ —these are the most commonly occurring salts—are readily soluble in cold water.

Use sodium salicylate,  $\text{C}_6\text{H}_4(\text{OH})\text{CO}_2\text{Na}$  or  $\text{Na} \cdot \text{C}_7\text{H}_5\text{O}_3$ .

**1. Concentrated Sulphuric Acid:** dissolves on warming; charring occurs slowly, accompanied by the evolution of carbon monoxide and sulphur dioxide.

**2. Concentrated Sulphuric Acid and Methyl Alcohol ("Oil of Winter-green" Test).**—When 0.5 gram of a salicylate or of salicylic acid is treated with a mixture of 1.5 ml. of concentrated sulphuric acid and 3 ml. of methyl alcohol and the whole gently warmed, the characteristic, fragrant odour of the ester, methyl salicylate (I) ("oil of winter-green"), is obtained. The odour is readily detected by pouring the mixture into dilute sodium carbonate solution contained in a porcelain dish.



**3. Dilute Hydrochloric Acid\*:** crystalline precipitate of salicylic acid from solutions of the salts. The precipitate is moderately soluble in hot water, from which it crystallises on cooling.

**4. Silver Nitrate Solution:** heavy, crystalline precipitate of silver salicylate  $\text{Ag} \cdot \text{C}_7\text{H}_5\text{O}_3$  from neutral solutions; it is soluble in boiling water and crystallises from the solution on cooling.



\* Or any other mineral acid.

**5. Ferric Chloride Solution:** intense violet-red coloration with neutral solutions of salicylates or with free salicylic acid; the colour disappears upon the addition of dilute mineral acids, but not of a little acetic acid. The presence of a *large* excess of many organic acids (acetic, tartaric and citric) prevents the development of the colour, but the addition of a few drops of dilute ammonia solution will cause it to appear.

**6. Dilute Nitric Acid.**—When a salicylate or the free acid is boiled with dilute nitric acid (1 : 5) and the mixture poured into 4 times its volume of cold water, a crystalline precipitate of 5-nitro-salicylic acid (I) is obtained. The precipitate is filtered off and recrystallised from boiling water; the acid, after drying, has a melting point of 226°.



Poly-nitro salicylic acids are formed when the concentration of nitric acid exceeds 2–3*N*. It must be emphasised that *nitro-salicylic acids may explode on strong heating*, and this must be borne in mind when removing salicylates by oxidation with nitric acid and evaporating to dryness prior to the precipitation of Group IIIA. If salicylate is suspected, it is probably best to remove it by acidifying the concentrated solution with dilute hydrochloric acid: most of the salicylic acid will separate out upon cooling.

**7. Soda Lime.**—When salicylic acid or one of its salts is heated with excess of soda lime in an ignition tube, phenol  $\text{C}_6\text{H}_5(\text{OH})$  is evolved, which may be recognised by its characteristic odour.



**8. Action of Heat.**—Salicylic acid, when gradually heated above its melting point, sublimes. If it is rapidly heated, it is decomposed into carbon dioxide and phenol (I). Salicylates char on heating and phenol is evolved.



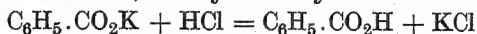
#### IV, 41. REACTIONS OF BENZOATES, $\text{C}_6\text{H}_5\cdot\text{CO}_2^-$ OR $\text{C}_7\text{H}_5\text{O}_2^-$

**Solubility.**—Benzoic acid,  $\text{C}_6\text{H}_5\cdot\text{CO}_2\text{H}$  or  $\text{H}\cdot\text{C}_7\text{H}_5\text{O}_2$ , is a white, crystalline solid; it has a melting point of 121° and sublimes at a somewhat higher temperature. The acid is sparingly soluble in cold water, but more soluble in hot water, from which it crystallises out on cooling; it is soluble in alcohol and in ether. All the benzoates, with the exception of the silver and basic ferric salts, are readily soluble in cold water.

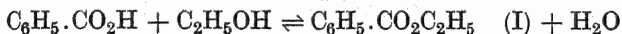
Use potassium benzoate,  $\text{C}_6\text{H}_5\cdot\text{CO}_2\text{K}$  or  $\text{K}\cdot\text{C}_7\text{H}_5\text{O}_2$ .

1. **Concentrated Sulphuric Acid:** no charring occurs on heating; the acid forms a sublimate on the sides of the test-tube and irritating fumes are evolved.

2. **Dilute Sulphuric Acid\*:** white, crystalline precipitate of benzoic acid from cold solutions of benzoates. The acid may be filtered off, dried between filter paper or upon a porous tile and identified by means of its melting point ( $121^{\circ}$ ). If the latter is somewhat low, it may be recrystallised from hot water.



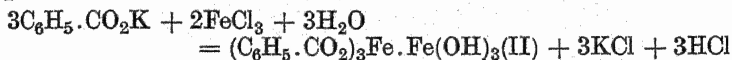
3. **Concentrated Sulphuric Acid and Ethyl Alcohol.**—Heat 0.5 gram of a benzoate or of benzoic acid with a mixture of 1.5 ml. of concentrated sulphuric acid and 3 ml. of ethyl alcohol for a few minutes. Allow the mixture to cool, and note the pleasant and characteristic aromatic odour of the ester, ethyl benzoate (I). The odour is more apparent if the mixture is poured into dilute sodium carbonate solution contained in an evaporating basin; oily drops of ethyl benzoate will separate out.



4. **Silver Nitrate Solution:** white precipitate of silver benzoate  $\text{Ag}\cdot\text{C}_7\text{H}_5\text{O}_2$  from neutral solutions. The precipitate is soluble in hot water and crystallises from the solution on cooling; it is also soluble in dilute ammonia solution.



5. **Ferric Chloride Solution:** buff-coloured precipitate of basic ferric benzoate (II) from neutral solutions. The precipitate is soluble in hydrochloric acid, with the simultaneous separation of benzoic acid (see reaction 2).



6. **Soda Lime.**—Benzoic acid and benzoates are decomposed when heated in an ignition tube with excess of soda lime into benzene  $\text{C}_6\text{H}_6$ , which burns with a smoky flame, and carbon dioxide, the latter combining with the alkali present.



7. **Action of Heat.**—When benzoic acid is heated in an ignition tube, it melts, sublimes and condenses in the cool parts of the tube. An irritating vapour is simultaneously evolved, but no charring occurs. If a little of the acid or of one of its salts is heated upon platinum foil or broken porcelain, it burns with a blue, smoky flame (distinction from succinate).

\* Or any other mineral acid.

IV, 42. REACTIONS OF SUCCINATES,  $C_4H_4O_4^{--}$ 

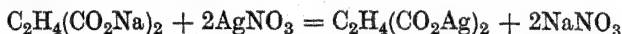
**Solubility.**—Succinic acid,  $HO_2C.CH_2.CH_2.CO_2H$  or  $H_2.C_4H_4O_4$  (a dibasic acid), is a white, crystalline solid with a melting point of  $182^\circ$ ; it boils at  $235^\circ$  with the formation of succinic anhydride  $C_4H_4O_3$  by the loss of one molecule of water. The acid is fairly soluble in water (68.4 grams per litre at  $20^\circ$ ), but more soluble in hot water; it is moderately soluble in alcohol and in acetone, slightly soluble in ether and sparingly soluble in chloroform. Most normal succinates are soluble in cold water; the silver, calcium, barium and basic ferric salts are sparingly soluble.

Use sodium succinate,  $C_2H_4(CO_2Na)_2$  or  $Na_2.C_4H_4O_4$ .

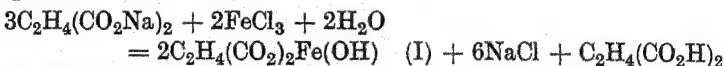
**1. Concentrated Sulphuric Acid.**—The acid or its salts dissolve in warm, concentrated sulphuric acid without charring; if the solution is strongly heated, slight charring takes place and sulphur dioxide is evolved.

Dilute sulphuric acid has no visible action.

**2. Silver Nitrate Solution:** white precipitate of silver succinate  $Ag_2.C_4H_4O_4$  from neutral solutions, readily soluble in dilute ammonia solution.



**3. Ferric Chloride Solution:** light-brown precipitate of basic ferric succinate (I) with a neutral solution; some free succinic acid is simultaneously produced, and the solution acquires an acid reaction.



**4. Barium Chloride Solution:** white precipitate of barium succinate  $Ba.C_4H_4O_4$  from neutral or slightly ammoniacal solutions (distinction from benzoate). Precipitation is slow from dilute solutions, but may be accelerated by vigorous shaking or by rubbing the inner wall of the test-tube with a glass rod.

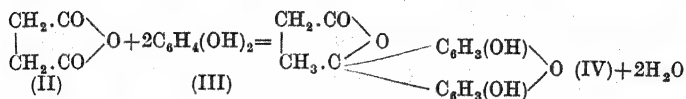


**5. Calcium Chloride Solution:** a precipitate of calcium succinate is very slowly produced from concentrated neutral solutions.

**6. Fluorescein Test.**—About 0.5 gram of the acid or one of its salts is mixed with 1 gram of resorcinol, a few drops of concentrated sulphuric acid added, and the mixture gently heated; a deep-red solution is formed. On pouring the latter into a large volume of water, an orange-yellow solution is obtained, which exhibits an intense green fluorescence. The addition of excess of sodium hydroxide solution intensifies the

fluorescence, and the colour of the solution changes to bright red.

Under the influence of concentrated sulphuric acid, succinic anhydride (II) is first formed, and this condenses with the resorcinol (III) to yield succinyl-fluorescein (IV).

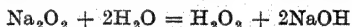


For the quinonoid structure, which is probably to be preferred, see the analogous formula for fluorescein in Section IV, 15, reaction 8.

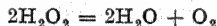
**7. Action of Heat.**—When succinic acid or its salts are strongly heated in an ignition tube, a white sublimate of succinic anhydride  $\text{C}_4\text{H}_4\text{O}_3$  is formed and irritating vapours are evolved. If the ignition is carried out on platinum foil or upon broken porcelain, the vapour burns with a non-luminous, blue flame, leaving a residue of carbon (distinction from benzoate).

#### IV, 43. REACTIONS OF HYDROGEN PEROXIDE, $\text{H}_2\text{O}_2$

This substance is marketed in the form of "10, 20, 40 and 100-volume" solutions. It is formed upon adding sodium peroxide in small portions to ice water:



Owing to the heat liberated in the reaction, part of the hydrogen peroxide is decomposed:



It is usually more convenient to employ a solution of hydrogen peroxide made alkaline with sodium hydroxide solution. A convenient source is the inexpensive sodium perborate  $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ ; this yields hydrogen peroxide when its aqueous solution is heated:



Use a dilute solution (say, 3 per cent) of hydrogen peroxide.

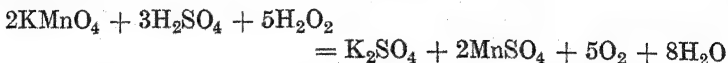
**1. "Perchromic Acid" Test.**—If an acidified solution of hydrogen peroxide is mixed with a little diethyl ether (*highly inflammable*), amyl alcohol or amyl acetate and a few drops of potassium dichromate solution added and the mixture gently shaken, the upper organic layer is coloured a beautiful blue. For further details, see Section IV, 33, reaction 4. The test will detect 0.1 mg. of hydrogen peroxide.

If ether is employed, a blank test must always be carried out with the ether alone because after standing it may contain organic peroxides which give the test. The peroxides may be removed by shaking 1 litre of ether with a solution containing 60 grams of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , 6 ml. of concentrated  $\text{H}_2\text{SO}_4$  and 110 ml. of water, then with chromic acid solution (to oxidise any acetaldehyde produced), washing with alkali and redistilling. The peroxides may also be removed by treatment with aqueous sodium sulphite. The use of amyl alcohol is, however, to be preferred.

**2. Potassium Iodide-Starch Test.**—If hydrogen peroxide is added to a solution containing potassium iodide and starch and acidified, a blue coloration of "starch iodide" appears.



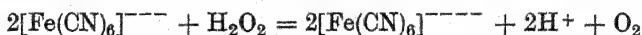
**3. Potassium Permanganate Solution:** decolourised in acid solution and oxygen is evolved.



**4. Titanic Sulphate Solution:** orange-red coloration (see under Titanium, Section IX, 12, reaction 6). This is a very delicate test.

The titanac sulphate solution may be prepared by heating titania with three times its volume of concentrated sulphuric acid, cooling, diluting cautiously with ice water and filtering, if necessary.

**5. Potassium Ferricyanide-Ferric Chloride Test.**—If a nearly neutral solution of pure ferric chloride is treated with a little pure potassium ferricyanide and the resulting yellow solution mixed with a nearly neutral solution of hydrogen peroxide, the mixture will assume a green coloration and then, on standing, Prussian blue will separate.

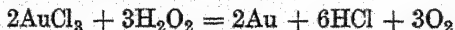


Other substances, *e.g.* stannous chloride, sodium sulphite and sodium thiosulphate, will reduce potassium ferricyanide to potassium ferrocyanide so that this reaction alone is not always a reliable test.

† The spot-test technique is as follows. In adjacent depressions of a spot plate place a drop of distilled water and a drop of the test solution. Add a drop of the reagent (equal volumes of 0.5 per cent ferric chloride solution and 0.8 per cent potassium ferricyanide solution) to each. A blue coloration or precipitate is formed.

Sensitivity: 0.1  $\mu\text{g. H}_2\text{O}_2$ . Concentration limit: 1 in 600,000.

**6. Gold Chloride Solution:** reduced to finely divided metallic gold, which appears greenish-blue by transmitted light and brown by reflected light.



† The spot-test technique is as follows. Mix a drop of the neutral test solution with a drop of 0.01 per cent gold chloride solution in a micro crucible and warm. After a short time, the solution is coloured red or blue with colloidal gold.

Sensitivity: 0.07  $\mu\text{g. H}_2\text{O}_2$ . Concentration limit: 1 in 700,000.



†7. **Lead Sulphate Test.**—Hydrogen peroxide converts black lead sulphide into white lead sulphate:



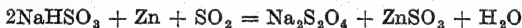
Place a drop of the neutral or slightly acid test solution upon drop reaction paper impregnated with lead sulphide. A white spot is formed on the brown paper.

Sensitivity: 0.04  $\mu\text{g}$ .  $\text{H}_2\text{O}_2$ . Concentration limit: 1 in 1,250,000.

The **lead sulphide paper** is prepared by soaking drop-reaction paper in a 0.05 per cent solution of lead acetate, exposing it to a little hydrogen sulphide gas and then drying in a vacuum desiccator. The paper will keep in a stoppered bottle.

#### IV, 44. REACTIONS OF HYDROSULPHITES (HYPOSULPHITES OR DITHIONITES), $\text{S}_2\text{O}_4^{--}$

Hydrosulphites are obtained by the action of reducing agents, such as zinc, upon acid sulphites:



Sulphur dioxide may also be passed into a cooled suspension of zinc dust in water:



The sodium salt may be obtained by double decomposition with sodium carbonate:



Sodium hydrosulphite is a powerful and important reducing agent. A solution of the salt containing excess of sodium hydroxide is used as an absorbent for oxygen in gas analysis.

Use sodium hydrosulphite,  $\text{Na}_2\text{S}_2\text{O}_4$ .

1. **Dilute Sulphuric Acid:** orange coloration, which soon disappears, accompanied by the evolution of sulphur dioxide and the precipitation of sulphur.



2. **Concentrated Sulphuric Acid:** immediate evolution of sulphur dioxide and the precipitation of pale yellow sulphur.

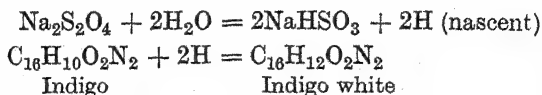
3. **Silver Nitrate Solution:** black precipitate of metallic silver.

4. **Copper Sulphate Solution:** red precipitate of metallic copper.

5. **Mercuric Chloride Solution:** grey precipitate of metallic mercury.

6. **Methylene Blue Solution:** immediate decolourisation in the cold. The methylene blue is reduced to the colourless leuco compound.

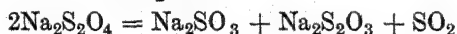
**7. Indigo Solution:** reduced to the colourless leuco compound, known as indigo white.



The **indigo solution** is prepared by digesting 2 grams of indigo with 10 grams of fuming sulphuric acid (*CAUTION*), and then pouring very slowly into 1 litre of 4 per cent sulphuric acid.

**8. Potassium Ferrous Ferrocyanide Test.**—Upon adding potassium ferrocyanide solution to a solution of a ferrous salt containing a little sodium hydrosulphite, a *white* precipitate of potassium ferrous ferrocyanide  $\text{K}_2\text{Fe}[\text{Fe}(\text{CN})_6]$  is produced (compare Section III, 19, reaction 6).

**9. Action of Heat.**—Upon heating sodium hydrosulphite, it suddenly evolves sulphur dioxide at about  $190^\circ$  (exothermic reaction). The residue has lost its reducing power to indigo and methylene blue solution, being a mixture of sodium sulphite and sodium thiosulphate.



#### IV, 45. SPECIAL TESTS FOR MIXTURES OF ACID RADICALS\*

**1. Carbonate in the presence of Sulphite.**—Sulphites, on treatment with dilute sulphuric acid, liberate sulphur dioxide which, like carbon dioxide, produces a turbidity with lime or baryta water. The dichromate test for sulphites is, however, not influenced by the presence of carbonates. To detect carbonates in the presence of sulphites, treat the solid mixture with dilute sulphuric acid and pass the evolved gases through a small wash-bottle or boiling tube containing potassium dichromate solution and dilute sulphuric acid. The solution will be turned green and the sulphur dioxide will, at the same time, be completely removed; the residual gas is then tested with lime or baryta water in the usual manner.

An alternative procedure is to add a little solid potassium dichromate or a small volume of 10-volume hydrogen peroxide solution to the mixture and then to warm with dilute sulphuric

\* Full experimental details of the various tests referred to in this section will be found under the reactions of the anions. Reference will be made to the " $\text{Na}_2\text{CO}_3$  prepared solution" and to the " $\text{Na}_2\text{CO}_3$  practically neutral solution" (see 20) as these are normally used in systematic analysis. A solution of the sodium salts of the various anions may, of course, be used in checking the procedures.

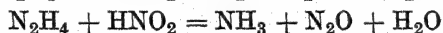
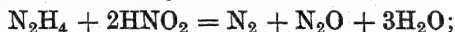
acid; the evolved gas is then passed through lime or baryta water.

**2. Nitrate in the presence of Nitrite.**—The nitrite is readily identified in the presence of a nitrate by treatment with dilute mineral acid, potassium iodide and starch paste (or potassium iodide–starch paper). The nitrate cannot, however, be detected in the presence of a nitrite since the latter gives the brown ring test with ferrous sulphate solution and *dilute* sulphuric acid. The nitrite is therefore completely decomposed first by one of the following methods:

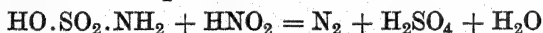
(i) Boil with ammonium chloride solution until effervescence ceases.\*

(ii) Warm with urea and dilute sulphuric acid until evolution of gas ceases.\*

(iii) Add the solution to solid hydrazine sulphate; reaction takes place in the cold, and the danger of slight oxidation of nitrite to nitrate is thereby avoided.



(iv) Add a little sulphamic acid to the solution:



The sulphamic acid procedure is probably the simplest and most efficient method for the removal of nitrite in aqueous solution.

The nitrate can then be tested for by the brown ring test.

**3. Nitrate in the presence of Bromide and Iodide.**—The brown ring test for nitrates cannot be applied in the presence of bromides and iodides since the liberation of the free halogen with concentrated sulphuric acid will obscure the brown ring due to the nitrate. The solution is therefore boiled with sodium hydroxide solution until ammonium salts, if present, are completely decomposed; powdered Devarda's alloy or aluminium powder (or wire) is then added and the solution gently warmed. The evolution of ammonia, detected by its smell and its action upon mercurous nitrate paper (see Section III, 36, reaction 1) and upon red litmus paper, indicates the presence of a nitrate.

An alternative method is to remove the halides by adding saturated silver sulphate solution. Since silver sulphate is only slightly soluble in water, it is better to use **ammoniacal silver sulphate solution**.

\* *Traces of nitrate are always formed in this reaction.*

This reagent contains  $[\text{Ag}(\text{NH}_3)_2]_2\text{SO}_4$  and provides a high concentration of silver ions: it is prepared by dissolving 7.8 grams of pure silver sulphate in 25 ml. of 4*N* ammonia solution and diluting to 100 ml. with water. The test solution is treated with sufficient of the reagent to precipitate all the halides; the silver halides are filtered off, a portion of the filtrate is carefully mixed with a five-fold excess of concentrated sulphuric acid, and the ferrous sulphate solution *cautiously* introduced down the side of the tube.

**4. Nitrate in the presence of Chlorate.**—The chlorate obscures the brown ring test. The nitrate is reduced to ammonia as described under 3; the chlorate is at the same time reduced to chloride, which may be tested for with silver nitrate solution and dilute nitric acid.

If a chloride is originally present, it may be removed first by the addition of silver sulphate solution or ammoniacal silver sulphate solution.

**5. Chloride in the presence of Bromide and/or Iodide.**  
—*Method A.* This procedure involves the removal of the bromide and iodide (but not chloride) by oxidation with potassium or ammonium persulphate in the presence of dilute sulphuric acid. The free halogens are thus liberated, and may be removed either by simple evaporation (addition of water may be necessary to maintain the original volume) or by evaporation at about 80° in a stream of air.

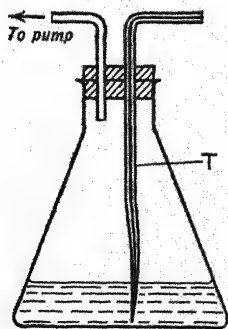
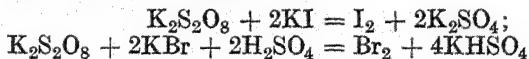


Fig. IV, 45, 1

Add solid potassium persulphate and dilute sulphuric acid to the "Na<sub>2</sub>CO<sub>3</sub> practically neutral solution" of the mixed halides contained in a conical flask; heat the flask to about 80°, and aspirate a current of air through the solution with the aid of a filter pump until the solution is colourless (Fig. IV, 45, 1; T is a drawn-out capillary tube). Add more potassium persulphate or water as may be found necessary. Test the residual colourless liquid for chloride with silver nitrate solution and dilute nitric acid.\*

\* Do not mistake precipitated silver sulphate for silver chloride. In a modification of this method, lead dioxide is substituted for potassium persulphate. Acidify the solution with acetic acid, add lead dioxide, and boil the mixture until bromine and iodine are no longer evolved. Filter, and test the filtrate, which should be colourless, with silver nitrate solution and dilute nitric acid.

*Method B.* Acidify the " $\text{Na}_2\text{CO}_3$  practically neutral solution" (see 20 below) of the halides with dilute nitric acid, add excess of silver nitrate solution, filter and wash until the washings no longer give the reactions of silver ions. Shake the precipitate with ammonium carbonate solution, filter and add a few drops of potassium bromide solution to the filtrate; a yellowish-white precipitate of silver bromide is obtained if a chloride is present.

The hydrolysis of the ammonium carbonate in aqueous solution gives rise to free dilute ammonia solution in which silver chloride, but not silver bromide or silver iodide, is appreciably soluble. The addition of bromide ions to the solution of silver chloride in ammonia results in the solubility product of silver bromide being exceeded, and precipitation occurs.

Alternatively, wash the precipitated halides until free from excess of silver nitrate solution, and then treat the precipitate with a cold, freshly prepared solution containing 4 per cent formaldehyde in 0.1*N* sodium carbonate solution: pour a little of the latter reagent through the filter several times. Test the filtrate for chloride with silver nitrate solution and dilute nitric acid. Silver bromide reacts slightly with the reagent yielding a faint opalescence; silver iodide is unaffected.

**6. Chloride in the presence of Bromide.**—Warm the solid mixture\* with a little potassium dichromate and concentrated sulphuric acid in a small distilling flask (Fig. IV, 2, 1), and pass the vapours, which contain chromyl chloride, into sodium hydroxide solution. Test for chromate, which proves the presence of a chloride, with hydrogen peroxide and amyl alcohol or with the diphenylcarbazine reagent.

**7. Chloride in the presence of Iodide.**—Add excess of silver nitrate solution to the " $\text{Na}_2\text{CO}_3$  practically neutral solution" (see 20) and filter; reject the filtrate. Wash the precipitate with dilute ammonia solution and filter again. Add dilute nitric acid to the washings; a white precipitate of silver chloride indicates the presence of chloride.

The separation is based upon the solubility of silver chloride in dilute ammonia solution and the practical insolubility of silver iodide in this reagent.

**8. Bromide and Iodide in the presence of each other and of Chloride.**—The presence of a chloride does not inter-

\* If a solution is being analysed, it should be evaporated to dryness before applying the test. Chlorates must, of course, be absent.

ferre with the reactions described below. To the " $\text{Na}_2\text{CO}_3$  prepared solution" strongly acidified with dilute hydrochloric acid add 1-2 drops of chlorine water (the solution obtained by carefully acidifying a dilute solution of sodium hypochlorite with dilute hydrochloric acid may also be used) and 2-3 ml. of chloroform or carbon tetrachloride; shake; a violet colour indicates iodide. Continue the addition of chlorine water or of acidified sodium hypochlorite solution *drop by drop* to oxidise the iodine to iodate and shake after each addition. The violet colour will disappear, and a reddish-brown coloration of the chloroform or carbon tetrachloride, due to dissolved bromine (and/or bromine monochloride  $\text{BrCl}$ ), will be obtained if a bromide is present. If iodide alone is present, the solution will be colourless after the violet colour has disappeared.

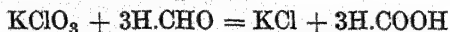
**9. Chloride, Chlorate and Perchlorate in the presence of each other.**—Each acid radical (anion) must be tested for separately. Divide the " $\text{Na}_2\text{CO}_3$  prepared solution" into 3 parts.

(i) *Chloride*. Acidify with dilute nitric acid and boil to expel carbon dioxide. Add silver nitrate solution; a white precipitate of silver chloride indicates the presence of chloride. Silver chlorate and perchlorate are soluble in water.

(ii) *Chlorate*. Any of the following methods may be used.

(a) Acidify with dilute nitric acid and add excess of silver nitrate solution; filter off the precipitated silver chloride. Now introduce a little chloride-free sodium nitrite (which reduces the chlorate to chloride) and more silver nitrate solution into the filtrate: a white, curdy precipitate of silver chloride indicates the presence of chlorate.

Alternatively, the reduction may be effected by heating the filtrate with a few ml. of 5-10 per cent formaldehyde solution: a white precipitate of silver chloride forms if a chlorate is present.



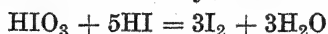
(b) Acidify with dilute sulphuric acid, add a little indigo solution followed by sulphurous acid solution: the indigo is bleached if a chlorate is present.

(iii) *Perchlorate*. Pass excess of sulphur dioxide into the solution to reduce chlorate to chloride, boil off the excess of sulphur dioxide, and precipitate the chloride with silver sulphate solution, afterwards removing the excess of silver with a solution of sodium carbonate. Evaporate the resulting solu-

tion to dryness and heat to dull redness (better in the presence of a little halide-free lime) to convert the perchlorate into chloride. Extract the residue with water, and test for chloride with silver nitrate solution and dilute nitric acid.

#### 10. Iodate and Iodide in the presence of each other.—

The addition of dilute acid to a mixture of iodate and iodide results in the separation of free iodine, due to the interaction between the liberated iodic and hydriodic acids.



Neither iodates nor iodides alone do this when acidified with dilute hydrochloric, sulphuric or acetic acids in the cold.

Test for iodide in the " $\text{Na}_2\text{CO}_3$  practically neutral solution" or in a solution of the sodium salts by the addition of a few drops of chlorine water (or acidified sodium hypochlorite solution) and 2–3 ml. of chloroform or carbon tetrachloride; the latter is coloured violet. Add excess of silver sulphate solution to another portion of the neutral solution and filter off the silver iodide; remove the excess of silver sulphate with sodium carbonate solution. Pass sulphur dioxide into the filtrate to reduce iodate to iodide, boil off the excess of sulphur dioxide, and add silver nitrate solution and dilute nitric acid. A yellow precipitate of silver iodide confirms the presence of iodate in the original substance.

#### 11. Phosphate in the presence of Arsenate.—

Both arsenate and phosphate give a yellow precipitate on warming with ammonium molybdate solution and nitric acid, the latter on gentle warming and the former on boiling.

Acidify the " $\text{Na}_2\text{CO}_3$  prepared solution" with dilute hydrochloric acid, pass in sulphur dioxide to reduce the arsenate to arsenite, boil off the excess of sulphur dioxide (test with potassium dichromate paper), and pass hydrogen sulphide into the solution to precipitate the arsenic as arsenious sulphide; continue the passage of hydrogen sulphide until no more precipitate forms. Filter, boil off the hydrogen sulphide, and test the filtrate for phosphate by the ammonium molybdate test or with the magnesium nitrate reagent.

An alternative method for the elimination of arsenate is the following. Acidify the " $\text{Na}_2\text{CO}_3$  prepared solution" with dilute hydrochloric acid and then add about one-quarter of the volume of concentrated hydrochloric acid (the total volume should be about 10 ml.). Add 0.5 ml. of 5 per cent ammonium iodide solution, heat to boiling, and pass hydrogen sulphide into the boiling solution until precipitation is complete (5–10

minutes). Filter off the arsenious sulphide, and boil off the hydrogen sulphide from the filtrate. Add ammonia solution until alkaline and excess of the magnesium nitrate reagent. A white precipitate indicates the presence of a phosphate.



**12. Phosphate, Arsenate and Arsenite in the presence of each other.**—Treat the “ $\text{Na}_2\text{CO}_3$  prepared solution” with dilute sulphuric acid until acidic, warm to expel carbon dioxide, render just alkaline with dilute ammonia solution and filter, if necessary. Add a few ml. of the magnesium nitrate reagent and allow to stand for 5–10 minutes: shake or stir from time to time. Filter off the white, crystalline precipitate of magnesium ammonium phosphate and/or magnesium ammonium arsenate (*A*), and keep the filtrate (*B*). Test for arsenite in the filtrate (*B*) by acidifying with dilute hydrochloric acid and passing hydrogen sulphide, when a yellow precipitate of arsenious sulphide is immediately produced if arsenite is present.

Wash the precipitate (*A*) with 0.5*N* ammonia solution, and remove half of it to a small beaker with the aid of a clean spatula. Treat the residue on the filter with a little silver nitrate solution containing a few drops of dilute acetic acid: a brownish-red residue (due to  $\text{Ag}_3\text{AsO}_4$ ) indicates arsenate present. If the residue is yellow (largely  $\text{Ag}_3\text{PO}_4$ ), pour 6*N* hydrochloric acid through the filter a number of times, and add a little potassium iodide solution and 1–2 ml. of chloroform or carbon tetrachloride to the extract and shake; if the organic layer acquires a purple colour, an arsenate is present.

Dissolve the white precipitate in the beaker in dilute hydrochloric acid, reduce the arsenate (if present) with sulphur dioxide or, better, with ammonium iodide solution (as described under 11), precipitate the arsenic as arsenious sulphide with hydrogen sulphide and boil off the hydrogen sulphide in the filtrate. Render the filtrate (*C*) slightly ammoniacal and add a little magnesium nitrate reagent: white, crystalline magnesium ammonium phosphate will be precipitated if a phosphate is present. Filter off the precipitate, wash with a little water, and pour a little silver nitrate solution (containing a few drops of dilute acetic acid) over it: yellow silver phosphate will be formed. Alternatively, the ammonium molybdate test may be applied to the filtrate (*C*) after evaporating to a small volume.



**13. Sulphide, Sulphite, Thiosulphate and Sulphate in the presence of each other.**—Upon the addition of dilute acid to the mixture, the hydrogen sulphide, liberated from the sulphide, and the sulphur dioxide, liberated from the sulphite and thiosulphate, react and sulphur is precipitated; this complication necessitates the use of a special procedure for their separation.

A mixture of the sodium salts or “ $\text{Na}_2\text{CO}_3$  prepared solution” is employed for this separation.

Shake the solution with excess of freshly precipitated  $\text{CdCO}_3$ , and filter.

**Residue.**  $\text{CdS}$  and excess of  $\text{CdCO}_3$ . Wash and reject washings. Digest residue with dilute acetic acid to remove excess of carbonate. A yellow residue indicates **sulphide**. Confirm by warming with dilute  $\text{HCl}$  and test the evolved  $\text{H}_2\text{S}$  with lead acetate paper.

**Filtrate.** Add  $\text{Sr}(\text{NO}_3)_2$  solution\* in slight excess, shake, allow to stand overnight and filter.

**Residue.**  $\text{SrSO}_3$  and  $\text{SrSO}_4$ . Wash, treat with dilute  $\text{HCl}$  and filter.

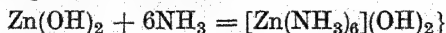
**Filtrate.** Contains  $\text{SrS}_2\text{O}_3$ . Acidify with dilute  $\text{HCl}$  and boil;  $\text{SO}_2$  is evolved and  $\text{S}$  is slowly precipitated.

**Thiosulphate present.**

**Residue.**  $\text{SrSO}_4$ . White.  
**Sulphate present.** Confirm by fusion with  $\text{Na}_2\text{CO}_3$  and apply sodium nitroprusside test.

**Filtrate.** Contains sulphurous acid. Add a few drops of a dilute solution of iodine; the latter is decolourised.†  
**Sulphite present.**

An alternative procedure for the **removal of the sulphide** is the following. Treat the solution of the sodium salts with a solution of zinc hexammine hydroxide  $[\text{Zn}(\text{NH}_3)_6](\text{OH})_2$  {prepared by adding ammonia solution to zinc nitrate solution until the initial precipitate of zinc hydroxide has redissolved, and then adding a further excess:



when zinc sulphide will be precipitated and is filtered off. The precipitate may be treated with dilute hydrochloric acid and a few drops of copper sulphate solution, when a black precipitate

\* Solubility in grams per litre:  $\text{SrS}_2\text{O}_3$ , 250 at  $13^\circ$ ;  $\text{SrSO}_3$ , 0.033 at  $17^\circ$ .

† Alternatively, add a few drops of fuchsin reagent; if it is decolourised, sulphite is present.

of cupric sulphide will indicate sulphide, or it may be tested for sulphide in the usual manner.

A simple method for **separating sulphite and sulphate** consists in acidifying the neutral solution of the alkali salts with dilute hydrochloric acid and adding excess of barium chloride solution; the sulphate is precipitated as barium sulphate and is removed by filtration. The production of a further precipitate of barium sulphate upon the addition to the filtrate of a little concentrated nitric acid or of bromine water and warming, proves the presence of sulphite.

**14. Sulphide, Sulphite and Thiosulphate in the presence of each other.**—It is assumed that the solution is slightly alkaline and contains the sodium salts of the anions, *e.g.* the " $\text{Na}_2\text{CO}_3$  prepared solution."

(i) Test a portion of the solution for sulphide with sodium nitroprusside solution. The formation of a purple coloration indicates the presence of a sulphide.

(ii) If sulphide is present, remove it by shaking with freshly precipitated cadmium carbonate and filter. Test a portion of the filtrate with sodium nitroprusside solution to see that all the sulphide has been removed. When no sulphide is present, treat the remainder of the filtrate with a drop of phenol-phthalein solution and pass in carbon dioxide until the solution is decolourised by it. Test 2–3 ml. of the colourless solution with 0.5–1 ml. of the fuchsin reagent. If the reagent is decolourised, the presence

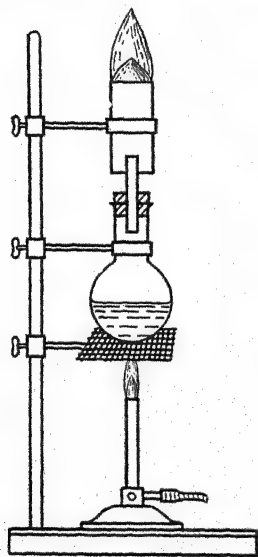


Fig. IV, 45, 2

of sulphite is indicated.

(iii) Treat the remainder of the colourless solution with dilute hydrochloric acid and boil for a few minutes. If sulphur separates, a thiosulphate is indicated. Alternatively, the nickel ethylenediamine nitrate test (Section IV, 5, reaction 9) may be applied.

**15. Borate in the presence of Copper and Barium Salts.**—When carrying out the ethyl borate test for borates (Section IV, 23, reaction 2), it must be remembered that copper and

barium salts may also impart a green colour to the alcohol flame. The test may be carried out in the following way when salts of either or both of these metals are present. The mixture of the borate, concentrated sulphuric acid and ethyl alcohol is placed in a small round-bottomed flask, fitted with a glass jet and surmounted by a wide glass tube, which acts as a "chimney" (Fig. IV, 45, 2). The mixture is gently warmed, and the vapours ignited at the top of the wide glass tube. A green flame confirms the presence of a borate.

An alternative procedure is given in Section VII, 3, test (ix).

**16. Fluoride, Silicofluoride and Sulphate in the presence of each other.**—The following differences in solubilities of the lead salts are utilised in this separation: lead silicofluoride is soluble in water; lead fluoride is insoluble in water but soluble in dilute acetic acid; lead sulphate is insoluble in water and in boiling dilute acetic acid, but soluble in concentrated ammonium acetate solution.

Add excess of lead acetate solution to the solution of the alkali metal salts, and filter cold.

**Residue.** Wash well with cold water.

Divide into two parts.

(i) *Smaller portion.* Add excess of dilute acetic acid and boil (this will dissolve any lead fluoride). White residue indicates **sulphate**. The residue is soluble in ammonium acetate solution.

(ii) *Larger portion.* Treat cautiously with concentrated sulphuric acid and test with a moist glass rod. Milkiness of the water and etching of the tube indicates **fluoride**.

**Filtrate.** Add  $\text{Ba}(\text{NO}_3)_2$  solution and warm gently. White crystalline precipitate indicates **silicofluoride**.

**17. Oxalate in the presence of Fluoride.**—Both calcium fluoride and calcium oxalate are precipitated by ammonium oxalate solution in the presence of dilute acetic acid. The fluoride may be identified in the usual manner with concentrated sulphuric acid or as described below. The oxalate is most simply detected by dissolving a portion of the precipitate in hot dilute sulphuric acid and then adding a few drops of a very dilute solution of potassium permanganate. The latter will be decolourised if an oxalate is present.

Use may be made of the fact that even solid calcium fluoride reacts with the zirconium-alizarin-S reagent (compare Section IV, 17, reaction 6) and, in consequence, the fluoride test may be carried out in the presence of oxalate and phosphate, which interfere in

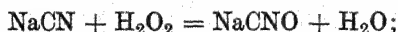
aqueous solution. The calcium salts are precipitated in neutral or faintly basic solution. The precipitate is ignited and digested with dilute acid. The residue is then tested for fluoride by adding a little of the zirconium-alizarin-S reagent: the red hue of the reagent disappears and a yellow coloration results.

The reagent is prepared by dissolving 0.05 gram of zirconyl nitrate in 10 ml. of concentrated hydrochloric acid and 50 ml. of water, and this solution is mixed with a solution of 0.05 gram of sodium alizarin sulphonate in 50 ml. of water.

### 18. Chloride and Cyanide in the presence of each other.

—Both silver chloride and silver cyanide are insoluble in water, but soluble in dilute ammonia solution. Three methods are available for the detection of cyanide in the presence of chloride.

(i) The concentrated solution, or preferably the solid mixture of sodium salts, is treated with about 5 times its weight of "100 volume" hydrogen peroxide and the mixture gently warmed; ammonia is evolved, which is recognised by its action upon mercurous nitrate paper. The solution is then boiled to decompose all the hydrogen peroxide, and then tested for chloride with silver nitrate solution and dilute nitric acid.



(ii) The cyanide is precipitated as the pale green nickel cyanide by the addition of excess of a solution of nickel sulphate to the neutral solution; the whole is filtered and the excess of nickel sulphate removed by boiling with sodium hydroxide solution and filtering off the precipitate of nickel hydroxide. The filtrate is acidified with dilute nitric acid and excess of silver nitrate solution added. A white, curdy precipitate of silver chloride confirms the presence of chloride.

(iii) The solution of the mixed sodium salts is treated with excess of solid sodium bicarbonate (see Fig. IV, 2, 1), the mixture warmed, and the evolved hydrogen cyanide passed into silver nitrate solution acidified with dilute nitric acid; a white precipitate of silver cyanide is obtained. This method can be employed in the presence of ferrocyanides, ferricyanides and thiocyanates.

For the detection of cyanide, chloride, bromide and iodide in the presence of one another the cyanide is first completely removed, and the separation of chloride, bromide and iodide carried out as detailed under 8.

The cyanide can also be detected by the usual Prussian blue

test or "ferri-thiocyanate" test (Section IV, 8, reactions 4 and 6).

### 19. Ferrocyanide, Ferricyanide and Thiocyanate in the presence of each other.

Acidify the " $\text{Na}_2\text{CO}_3$  practically neutral solution" of the sodium salts with acetic acid, add excess of a solution of thorium nitrate and a little Gooch asbestos and shake well; filter.

**Residue.**  $\text{Th}[\text{Fe}(\text{CN})_6]$  and asbestos (the latter is added to facilitate filtration of the gelatinous precipitate).<sup>\*</sup> Wash with a little cold water. Treat the ppt. on the filter paper with dilute  $\text{NaOH}$  solution; acidify the alkaline extract with dilute  $\text{HCl}$  and add a few drops of  $\text{FeCl}_3$  solution.

A precipitate of Prussian blue indicates ferrocyanide.

**Filtrate.** Add  $\text{CdSO}_4$  solution and a little Gooch asbestos, shake, filter.

**Residue.** Orange.  $\text{Cd}_3[\text{Fe}(\text{CN})_6]_2$  and asbestos. Extract with  $\text{NaOH}$  solution, acidify extract with dilute  $\text{HCl}$ , add freshly prepared  $\text{FeSO}_4$  solution. Ppt. of Prussian blue indicates ferri-cyanide.

**Filtrate.** Add  $\text{FeCl}_3$  solution and ether. Red coloration of ether proves presence of thiocyanate.

**20. Separation of Organic Acids (Oxalate, Tartrate, Citrate, Benzoate, Succinate, Acetate, Formate and Salicylate in the presence of each other).**—Intimately mix the mixture of acids and/or their salts with 3–4 times the bulk of anhydrous sodium carbonate, add just sufficient water to dissolve the sodium carbonate, heat under reflux for 15 minutes, and filter. Wash and neglect the residue. The filtrate will be termed the " $\text{Na}_2\text{CO}_3$  prepared solution." Treat the combined filtrate and washings with dilute nitric acid a little at a time with stirring until acid (use litmus paper test), boil gently to expel carbon dioxide and allow to cool. Add dilute ammonia solution portionwise and with stirring until just alkaline. Filter, if not clear. It is advisable to boil gently for a minute or two to remove any appreciable excess of ammonia. The resulting solution will be free from heavy metals and almost neutral. It will be referred to as the " $\text{Na}_2\text{CO}_3$  practically neutral solution."<sup>†</sup>

<sup>\*</sup> Filter paper pulp (e.g. in the form of a Whatman filtration accelerator) cannot be used as the organic matter may cause appreciable reduction of the ferricyanide.

<sup>†</sup> See Section VII, 17, tests 4 and 5 for a slightly modified procedure.

Add  $\text{CaCl}_2$  solution to the cold " $\text{Na}_2\text{CO}_3$  practically neutral solution," rub sides of vessel with a glass rod, allow to stand for 10 minutes with occasional shaking; filter.

<b>Residue.</b> May be Ca oxalate (formed immediately) or Ca tartrate (formed on standing).* Wash. Boil with dilute acetic acid and filter.		<b>Filtrate.</b> Add more $\text{CaCl}_2$ solution, boil under reflux for at least 5 minutes. A ppt. may form gradually; filter.	
<b>Residue.</b> $\text{CaC}_2\text{O}_4$ . Dissolve in a little dilute $\text{HCl}$ , add $\text{NH}_3$ solution in slight excess. White ppt. insoluble in dilute acetic acid. <b>Oxalate present.</b> Confirm by resorcinol test, or by decolourisation of a dilute solution of acidified $\text{KMnO}_4$ at $60-70^\circ$ .	<b>Filtrate.</b> May contain Ca tartrate. Test neutral solution with Fenton's reagent, violet coloration (see Note), or by silver mirror test for tartrate. Confirm by copper hydroxide test.	<b>Residue.</b> Ca citrate. White. <b>Citrate present.</b> Divide into 2 parts. (i) Confirm by Denigès' test. (ii) Dissolve in dilute $\text{HCl}$ , convert into neutral solution with $\text{NH}_3$ solution, etc., and add $\text{CdCl}_2$ solution. White gelatinous precipitate.	<b>Filtrate.</b> If citrate present, evaporate to dryness on water bath, add a little cold water, and filter from any residue of Ca citrate. If citrate absent, proceed with solution. Add $\text{FeCl}_3$ solution; filter (if necessary).
		<b>Residue.</b> Ferric benzoate and/or ferric succinate. Separate by procedure A.	<b>Filtrate.</b> Coloured. Dilute, boil and filter.
		<b>Residue.</b> Basic ferric formate and basic ferric acetate. Separate by procedure B.	<b>Filtrate.</b> Coloured. Coloured. (a) Violet—salicylate. Confirm by "oil of winter-green" test. (b) Deep blue or greenish black—gallate or tannate.†

*Note.*—With Fenton's reagent and a neutral solution of a citrate, a yellow or brown colour is obtained, but there is no precipitation of iron; with an oxalate, the iron is precipitated as the hydroxide.

### Procedure A

**Separation of benzoate and succinate.**—Boil the precipitated ferric salts with a little dilute ammonia solution, filter off

\* It must be remembered that phosphates, fluorides, sulphates, etc., are precipitated by calcium chloride solution.

† Gallates and tannates are of rare occurrence in general qualitative analysis.

the precipitated ferric hydroxide and discard the precipitate; boil off the excess of ammonia from the filtrate. Divide the filtrate into two parts.

Treat one portion with barium chloride solution and filter off precipitate formed. The residue consists of barium *succinate*. Confirm the succinate by the fluorescein test. Acidify the second portion of the filtrate with dilute hydrochloric acid, when *benzoic acid* will separate out on cooling. It can be identified by its melting point.

### Procedure B

#### Formates and Acetates in the presence of each other.—

**Formate.** (i) *In the absence of tartrates, citrates and reducing agents.* Add silver nitrate solution to the " $\text{Na}_2\text{CO}_3$  practically neutral solution"; a white precipitate, which is converted into a black deposit of silver on boiling, indicates *formate*. A little of the solid substance may be treated with concentrated sulphuric acid, when carbon monoxide (burns with blue flame) will be evolved in the cold.

(ii) *In the presence of tartrates, citrates and reducing agents.* Acidify the mixture with dilute sulphuric acid and distil. A solution of formic and acetic acids will pass over. Neutralise distillate with dilute ammonia solution, boil off excess of ammonia (if necessary) and test as in (i).

**Acetate.** If other organic acids are present, obtain the solution of mixed acids as in (ii); otherwise, use the " $\text{Na}_2\text{CO}_3$  practically neutral solution." Boil under reflux with an equal volume of potassium dichromate solution and dilute sulphuric acid; this will decompose the formic acid. Distil off the acetic acid, neutralise and test with ferric chloride solution.

If the solid is available, the cacodyl test may be employed.

For other methods of separation and detection of selected anions, see Section VII, 17, Tables A and C.

## CHAPTER V

### SYSTEMATIC MACRO QUALITATIVE INORGANIC ANALYSIS FOR ELEMENTARY STUDENTS\*

It is assumed that the student is already familiar with the operations (ignition tests, blowpipe tests, flame tests, borax bead tests, precipitation, filtration, etc.) described in Chapter II (Sections II, 1 and II, 2). For the cations, a limited number of preliminary reactions should first be studied, followed by the analysis of a mixture or solution containing a member or members of each group. This will provide practice at the very outset in the use of the Group Separation Tables. The volume of the initial solution should be kept as small as possible (1 ml. is a convenient volume) as should also the weight of solid used (say,  $>0.5$  gram). The student should pay particular attention to (i) the exact experimental conditions for the reaction, (ii) the colour and physical characteristics (*e.g.* whether crystalline, amorphous or gelatinous) of each precipitate and (iii) the solubility of each precipitate in excess of the precipitant, or in solutions of other reagents. He should, as far as possible, represent the chemical reactions by ionic equations and then check his own equations against the molecular equations given in the text. This will give the student excellent practice in writing and balancing equations, and also help to impress the reactions upon his (or her) memory.

**Droppers.**—The so-called “medicine droppers” and also the similar dropper pipettes (the latter have a longer tip) may be purchased and are inexpensive. They are very useful for adding small volumes of reagents (particularly dropwise) and also for washing precipitates. If calibrated, say at 0.5 ml. intervals, droppers may be employed for measuring small volumes. The rubber teat (bulb) should be removed and the

\* This chapter has been retained in the present edition as it appears to meet the wishes of numerous correspondents. It covers the requirements of those who desire a brief introductory course and have only a limited time at their disposal. Additional anions (*e.g.* fluoride, borate and phosphate) can be readily introduced if required. The abbreviated course will be found suitable for the General Certificate of Education (Advanced Level), for the Intermediate Science Examinations of the various Universities, for the Ordinary National Certificate in Chemistry, and for examinations of similar scope.



glass tube thoroughly rinsed with distilled water immediately after use.

Droppers can be readily made by the student as follows. Draw out a length of glass tubing (about 20 cm. long and of about 7 mm. diameter) in the centre by suitably heating in a flame: the narrow part of the tube should be about 3 mm. external diameter. Cut the tube in the middle of the drawn-out portion, and thus obtain two jets. Heat the wider end and enlarge it with the aid of a file so that it will securely hold a rubber teat (bulb). The teat should be of such size that liquid cannot be drawn into it. The dropper may be calibrated by holding it vertically after filling with distilled water and allowing the water to flow dropwise into a small measuring cylinder: 0.5 ml. intervals should be marked by means of a file or "glass" pencil. The number of drops (preferably about 20 per ml.) should also be determined.

**V, 1. Abbreviated Course of Instruction.**—The following preliminary reactions should be carried out by the student.

### REACTIONS OF THE CATIONS

**Pb<sup>++</sup>.** Section III, 2, reactions 1, 2, 3, 4; blowpipe test.

**Hg<sub>2</sub><sup>++</sup>.** Section III, 3, reactions 1, 6, 7.

**Ag<sup>+</sup>.** Section III, 4, reactions 1, 2, 3; blowpipe test.

Identification of a metal in the solution supplied by the teacher by means of Table I (Section III, 5).

**Hg<sup>++</sup>.** Section III, 6, reactions 1, 2, 3; dry test.

**Bi<sup>+++</sup>.** Section III, 7, reactions 1, 3, 5, 6, 10.

**Cu<sup>++</sup>.** Section III, 8, reactions 1, 2, 3, 4, 5, 8; dry test.

**Cd<sup>++</sup>.** Section III, 9, reactions 1, 3, 4; dry test.

Identification of a metal or metals in the solution supplied by means of Table II or IIA (Section III, 10).

**As (ous).** Section III, 11, reactions 1, 2, 3.

**As (ic).** Section III, 12, reactions 1, 2, 3, 4.

**Sb (ous).** Section III, 14, reactions 1, 2, 8.

**Sn<sup>++</sup>.** Section III, 16, reactions 1, 2, 3.

**Sn<sup>++++</sup>.** Section III, 17, reactions 1, 3, 4.

Identification of a metal or metals in the solution supplied by means of Table III or IIIA (Section III, 18).

**Fe<sup>++</sup>.** Section III, 19, reactions 1, 2, 3, 4, 6, 7, 8.

**Fe<sup>+++</sup>.** Section III, 20, reactions 1, 2, 3, 4, 5, 6, 10.

**Al<sup>+++</sup>.** Section III, 21, reactions 1, 2, 3, 7; dry test.

**Cr<sup>+++</sup>.** Section III, 22, reactions 1, 2, 3, 6; dry test (iii).

Identification of a metal or metals in the solution supplied by means of Table IV (Section III, 23).

**Co<sup>++</sup>.** Section III, 24, reactions 1, 2, 3, 5, 6, 7; dry test (ii).

**Ni<sup>++</sup>.** Section III, 25, reactions 1, 2, 3, 6, 7, 8; dry test (ii).

**Mn<sup>++</sup>.** Section III, 26, reactions 1, 2, 3, 5, 7; dry test (ii).

**Zn<sup>++</sup>.** Section III, 27, reactions 1, 2, 3, 6, 8, 9; dry test.

Identification of a metal or metals in the solution supplied by means of Table V (Section III, 28).

**Ba<sup>++</sup>.** Section III, 29, reactions 1, 2, 3, 4, 6; dry test.

**Sr<sup>++</sup>.** Section III, 30, reactions 1, 2, 3, 5, 6; dry test.

**Ca<sup>++</sup>.** Section III, 31, reactions 1, 2, 3, 5, 6; dry test.

Identification of a metal or metals in the solution supplied by means of Table VI (Section III, 32).

**Mg<sup>++</sup>.** Section III, 33, reactions 1, 2, 3, 5, 7, 8; dry test.

**K<sup>+</sup>.** Section III, 34, reaction 1; dry test.

**Na<sup>+</sup>.** Section III, 35, reaction 1; dry test.

**NH<sub>4</sub><sup>+</sup>.** Section III, 36, reactions 1, 3, 7; dry test.

Identification of a metal or metals in the solution supplied by means of Table VII (Section III, 37).

### REACTIONS OF THE ANIONS

**CO<sub>3</sub><sup>--</sup>.** Section IV, 2, reactions 1, 2.

**HCO<sub>3</sub><sup>-</sup>.** Section IV, 3, reactions (i), (ii), (iii).

**SO<sub>3</sub><sup>-</sup>.** Section IV, 4, reactions 1, 2, 4, 5, 9, 10.

**S<sub>2</sub>O<sub>3</sub><sup>--</sup>.** Section IV, 5, reactions 1, 2, 3, 6, 8.

**S<sup>--</sup>.** Section IV, 6, reactions 1, 2, 3, 5, 6.

**NO<sub>2</sub><sup>-</sup>.** Section IV, 7, reactions 1, 2, 7, 10.

**\*SCN<sup>-</sup>.** Section IV, 10, reactions 1, 2, 3, 6.

**Cl<sup>-</sup>.** Section IV, 14, reactions 1, 2, 3.

**Br<sup>-</sup>.** Section IV, 15, reactions 1, 2, 3, 5, 8.

**I<sup>-</sup>.** Section IV, 16, reactions 1, 2, 4, 7.

**F<sup>-</sup>.** Section IV, 17, reactions 1, 2, 6.

**NO<sub>3</sub><sup>-</sup>.** Section IV, 18, reactions 1, 2, 3, 4.

**\*ClO<sub>3</sub><sup>-</sup>.** Section IV, 19, reactions 1, 2, 3, 7, 10.

**SO<sub>4</sub><sup>--</sup>.** Section IV, 24, reactions 1, 2, 5, 6.

**PO<sub>4</sub><sup>---</sup>.** Section IV, 28, reactions 1, 3, 4, 5, 6.

**CrO<sub>4</sub><sup>--</sup>.** Section IV, 33, reactions 1, 2, 4, 5, 6.

**\*C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup> (acetate).** Section IV, 35, reactions 1, 2, 3, 4, 6.

**\*C<sub>2</sub>O<sub>4</sub><sup>--</sup> (oxalate).** Section IV, 37, reactions 1, 2, 3, 4.

### V. 2. Systematic Analysis. General Considerations.—

The student must realise that the object of qualitative analysis is not simply to detect the constituents of a given mixture; an equally important aim is to ascertain the approximate relative amounts of each component. For this purpose about 0.5 gram of material is usually employed for the analysis: the relative magnitudes of the various precipitates will provide a rough guide as to the proportions of the constituents present.

\* To be studied at the discretion of the teacher.

Every analysis is divided into three parts :

(1) *The preliminary examination.* This includes preliminary examination by dry tests, examination of the volatile products with sodium hydroxide solution (for ammonium), and with dilute and concentrated sulphuric acid (for acid radicals or anions). A special preliminary test for nitrate and/or nitrite is also made here.

(2) *The examination for acid radicals (or anions) in solution.*

(3) *The examination for metal ions (or cations) in solution.*

### V, 3. PRELIMINARY TESTS

**Test (i). Heating in a closed tube.**—Place about 0.1 gram of the substance in a dry ignition tube so that none of it remains adhering to the sides and heat cautiously; the tube should be held in an almost horizontal position. Raise the temperature gradually and carefully note any changes which take place.

[Table on p. 434]

**Test (ii). Charcoal block reductions.**

(a) Heat a little of the substance (*ca.* 0.1 gram) in a small cavity in a charcoal block in a blowpipe flame.

<i>Observation</i>	<i>Inference</i>
1. The substance decrepitates.	Crystalline salts, <i>e.g.</i> NaCl, KCl. Oxidising agents, <i>e.g.</i> nitrates, nitrites and chlorates. Apply test (b) below.
2. The substance deflagrates.	
3. The substance is infusible or incandescent, or forms an incrustation upon the charcoal.	

(b) Mix the substance (*ca.* 0.1 gram) with twice its bulk of anhydrous sodium carbonate, place it in a cavity in a charcoal block and heat in the reducing flame of the blowpipe.

<i>Observation</i>	<i>Inference</i>
1. Incrustation without metal: White, yellow when hot. White, garlic odour. Brown.	ZnO. As <sub>2</sub> O <sub>3</sub> . CdO.
2. Incrustation with metal: White incrustation; brittle metal. Yellow incrustation; brittle metal. Yellow incrustation; grey and soft metal, marks paper.	Sb. Bi. Pb.
3. Metal without incrustation: Grey metallic particles, attracted by magnet. Malleable beads.	Fe, Ni, Co. Ag and Sn (white); Cu (red flakes).

Observation	Inference
<p>(a) <b>A gas or vapour is evolved.</b></p> <ol style="list-style-type: none"> <li>1. Water is evolved; test with litmus paper.  The water is alkaline. The water is acid.</li> <li>2. Oxygen is evolved (rekindles a glowing splint).</li> <li>3. Nitrous oxide (rekindles glowing splint) and steam are evolved.</li> <li>4. Dark brown or reddish fumes (oxides of nitrogen); acidic in reaction.</li> <li>5. Carbon dioxide is evolved (lime water is rendered turbid).</li> <li>6. Ammonia is evolved (turns red litmus paper blue).</li> <li>7. Sulphur dioxide is evolved (odour of burning sulphur; turns potassium dichromate paper green; decolourises fuchsin solution).</li> <li>8. Hydrogen sulphide is evolved (odour of rotten eggs; turns lead acetate paper black or cadmium acetate paper yellow).</li> <li>9. Chlorine is evolved (yellowish-green gas; bleaches litmus paper; turns potassium iodide-starch paper blue); <i>very poisonous</i>.</li> <li>10. Bromine is evolved (reddish-brown vapour; choking odour; turns fluorescein paper red).</li> <li>11. Iodine is evolved (violet vapours condensing to black crystals).</li> </ol>	<p>Compounds with water of crystallisation (often accompanied by change of colour), ammonium salts, acid salts and hydroxides. Ammonium salts. Readily decomposable salts of strong acids. Nitrates, chlorates and certain oxides. Ammonium nitrate or nitrate mixed with an ammonium salt. Nitrates or nitrites of heavy metals. Carbonates or bicarbonates.  Ammonium salts.  Normal and acid sulphites; thiosulphates; certain sulphates.  Hydrated sulphides or sulphides in the presence of water.  Unstable chlorides, <i>e.g.</i> of copper; chlorides in the presence of oxidising agents.  Sources similar to chlorine.  Free iodine and certain iodides.</p>
<p>(b) <b>A sublimate is formed.</b></p> <ol style="list-style-type: none"> <li>1. White sublimate.*</li> <li>2. Grey sublimate, easily rubbed to globules.</li> <li>3. Steel-grey sublimate; garlic odour.</li> <li>4. Yellow sublimate.</li> </ol>	<p>Ammonium and mercuric salts; <math>\text{As}_2\text{O}_3</math>; <math>\text{Sb}_2\text{O}_3</math>. <i>Hg</i>.  <i>As</i>. <i>S</i> (melts on heating), <math>\text{As}_2\text{S}_3</math>, <math>\text{HgI}_2</math> (red when rubbed with a glass rod).</p>
<p>* If a white sublimate forms, heat with four times the bulk of anhydrous <math>\text{Na}_2\text{CO}_3</math> and a little KCN in an ignition tube. A grey mirror, convertible into globules on rubbing with a glass rod, indicates <i>Hg</i> (Note: <i>Hg</i> vapour is <i>very poisonous</i>); a brownish-black mirror, yielding a white sublimate and an odour of garlic when heated in a wide tube, indicates <i>As</i>; ammonia evolved (test with mercurous nitrate paper) indicates <i>ammonium salts</i>.</p>	

**Test (iii). Flame colorations.**—Place a small quantity of the substance (*ca.* 0.05 gram) on a watch glass, moisten with a little concentrated hydrochloric acid and introduce a little of the substance on a *clean* platinum wire into the base of the non-luminous Bunsen flame. An alternative method is to dip the platinum wire into concentrated hydrochloric acid contained in a watch glass or test-tube and then into the substance; sufficient will adhere to the platinum wire for the test to be carried out.

<i>Observation</i>	<i>Inference</i>
Persistent golden-yellow flame.	Na.
Violet (lilac) flame (crimson through cobalt-blue glass).	K.
Brick-red (yellowish-red) flame.	Ca.
Crimson flame.	Sr.
Yellowish-green flame.	Ba.
Livid-blue flame (wire slowly corroded).	Pb, As, Sb, Bi, Cu.

The sodium flame masks that of other elements, *e.g.* that of potassium. Mixtures can be readily detected with a direct-vision spectroscope. A less delicate method is to view the flame through two thicknesses of cobalt-blue glass, whereby the yellow colour due to sodium is masked or absorbed; potassium then appears crimson.

**Test (iv). Borax bead reactions.**—Make a borax bead in a loop of platinum wire by dipping the hot wire into borax and heating until colourless and transparent. Bring a *minute* quantity of the substance into contact with the hot bead and heat in the outer or oxidising flame. Observe the colour when the bead is hot and also when it is cold. Heat the bead in the inner or reducing flame and observe the colour in the hot and cold states. Coloured beads are obtained with compounds of copper, iron, chromium, manganese, nickel and cobalt; the most characteristic result is for cobalt.

<i>Oxidising flame</i>	<i>Reducing flame</i>	<i>Metal</i>
1. Green when hot; blue when cold.	Colourless when hot or opaque-red when cold.	Cu.
2. Yellow, hot and cold.	Green, hot and cold.	Fe.
3. Dark yellow when hot, green when cold.	Green, hot and cold.	Cr.
4. Violet (amethyst), hot and cold.	Colourless, hot and cold.	Mn.
5. Blue, hot and cold.	Blue, hot and cold.	Co.
6. Reddish-brown when cold.	Grey when cold.	Ni.

**Test (v). Test for the ammonium radical.**—Boil about 0.2 gram of the substance with 2–3 ml. sodium hydroxide solution. The evolution of ammonia, detected by its odour, its action upon litmus paper and upon mercurous nitrate paper, indicates the presence of an **ammonium salt**.

In order to avoid the necessity of holding the test-paper (litmus, etc.) in the vapour, the following simple device may be used. A test-tube is fitted with a cork carrying a wide tube (at least half the diameter of the test-tube) about 5 cm. long; the bottom of the wide tube should protrude just below the cork (Fig. VII, 2, 1). A test-paper can then be supported in the wide tube by simply folding it slightly over the upper edge of the glass tube. This device is recommended for all reactions on the macro scale in which evolved gases are identified by means of test-papers.

*Note.*—Sodium hydroxide is a dangerous substance because of its destructive action upon the eyes. Great care should be taken that the test-tube containing the hot sodium hydroxide solution is directed away from the eyes of the observer and of near neighbours.

**Test (vi). Test for nitrate (or nitrite).**—If ammonium is found, continue boiling until ammonia can no longer be detected by its action upon red litmus paper or upon mercurous nitrate paper; it may be necessary to add a further 2–3 ml. of sodium hydroxide solution. Then add a little zinc dust or aluminium powder or finely powdered Devarda's alloy (Cu, 50 per cent; Al, 45 per cent; Zn, 5 per cent) and warm the mixture gently. Remove the flame as soon as evolution of hydrogen commences and allow the reduction to proceed (the reaction may become vigorous with aluminium powder and cooling with tap water may be necessary to moderate the vigour of the reaction; alternatively, thin aluminium foil may be used). If ammonium is absent, add zinc dust or aluminium powder or Devarda's alloy to the reaction mixture from test (v). If ammonia is evolved, as detected by its action upon red litmus paper or upon filter paper moistened with mercurous nitrate solution, then the presence of *nitrate* or *nitrite* is indicated. The presence of nitrite will generally also be detected in the reaction with dilute sulphuric acid {see test (vii)}; if nitrite is absent, then the presence of nitrate alone is established.

It must be emphasised that the mercurous nitrate paper test for ammonia is not applicable in the presence of arsenites. Arsenites are reduced under the above conditions to arsine, which also blackens mercurous nitrate paper. Similar remarks apply to the tannic acid-silver nitrate test (Section III, 36, reaction 7).

**Test (vii). Action of dilute sulphuric acid.**—Treat about 0.2 gram of the substance in a test-tube with 2–3 ml. dilute (2*N*) sulphuric acid and note whether any reaction takes place in the cold (indicated by *C*). Warm gently and observe the effect produced.

Observation	Inference
1. Colourless gas is evolved with effervescence; gas is odourless and produces a turbidity when passed into lime water (see Fig. IV, 2, 1). ( <i>C</i> )	CO <sub>2</sub> from <i>carbonate</i> or <i>bicarbonate</i> .
2. Nitrous fumes evolved; recognised by reddish-brown colour and odour. ( <i>C</i> )	NO <sub>2</sub> from <i>nitrite</i> .
3. Yellowish-green gas evolved; suffocating odour, reddens then bleaches litmus paper, also turns starch-KI paper blue; <i>very poisonous</i> . ( <i>C</i> )	Cl <sub>2</sub> from <i>hypochlorite</i> .
4. Colourless gas evolved with suffocating odour; turns filter paper moistened with K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> solution green; decolourises fuchsin solution.	SO <sub>2</sub> from <i>sulphite</i> .
5. Colourless gas evolved; gives above tests for SO <sub>2</sub> ; sulphur is deposited in the solution.	SO <sub>2</sub> and S from <i>thio-sulphate</i> .
6. Colourless gas evolved; odour of rotten eggs; blackens filter paper moistened with lead acetate solution; turns cadmium acetate paper yellow.	H <sub>2</sub> S from <i>sulphide</i> .*
7. Odour of vinegar.	H. C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> from <i>acetate</i> .
8. Colourless gas is evolved; rekindles glowing splint.	O <sub>2</sub> from <i>peroxides</i> or <i>per-salts</i> of alkali and alkaline earth metals.
9. Upon boiling, yellow solution formed and SO <sub>2</sub> (fuchsin solution test, etc.) evolved.	SO <sub>2</sub> , etc., from <i>thio-cyanate</i> .

**Test (viii). Action of concentrated sulphuric acid.**—Treat about 0.2 gram of the substance with 2–3 ml. of concentrated sulphuric acid and warm the mixture gently, and incline the mouth of the test-tube away from you. (If chlorate is suspected from the preliminary charcoal reduction test to be present, use a very small quantity (less than 0.05 gram) for this test, as a dangerous explosion may result on warming.)

If the substance reacted with dilute sulphuric acid, the addition of concentrated sulphuric acid may result in vigorous reaction and rapid evolution of gas, which may be accompanied by a very fine spray of acid. In such a case, it is best to add dilute sulphuric acid dropwise (best with a clean dropper) to another portion of the substance until action ceases, and then to add 3–4 ml. of concentrated sulphuric acid.

\* Many sulphides, especially native ones, are not affected by dilute H<sub>2</sub>SO<sub>4</sub>; some H<sub>2</sub>S is evolved upon warming with concentrated HCl alone or with a little tin.

The following results may be obtained.

Observation	Inference
1. Colourless gas evolved with pungent odour and which fumes in the air; white fumes of $\text{NH}_4\text{Cl}$ in contact with glass rod moistened with concentrated $\text{NH}_3$ solution; $\text{Cl}_2$ evolved on addition of $\text{MnO}_2$ (reddens, then bleaches litmus paper).	HCl from <i>chloride</i> .
2. Gas evolved with pungent odour, reddish colour and fumes in moist air; on addition of $\text{MnO}_2$ increased amount of red fumes with odour of $\text{Br}_2$ (fumes colour filter paper moistened with fluorescein solution red).	HBr and $\text{Br}_2$ from <i>bromide</i> .
3. Violet vapours evolved, accompanied by pungent acid fumes, and often $\text{SO}_2$ and even $\text{H}_2\text{S}$ .	HI and $\text{I}_2$ from <i>iodide</i> .
4. Pungent acid fumes evolved, often coloured brown by $\text{NO}_2$ ; colour deepens upon addition of copper turnings (if nitrite absent).	$\text{HNO}_3$ and $\text{NO}_2$ from <i>nitrate</i> .
5. Yellow gas evolved in the cold with characteristic odour; explosion or crackling noise on warming <i>gently</i> (DANGER!).	$\text{ClO}_2$ from <i>chlorate</i> .
6. "Oily" appearance of tube in cold; on warming, pungent gas evolved, which corrodes the glass; if moistened glass rod introduced into the vapour, a gelatinous precipitate of hydrated silica is deposited upon it.	HF from <i>fluoride</i> .
7. Colourless gas evolved; burns with a blue flame; no charring ( <i>very poisonous</i> ).	CO from <i>formate</i> .
8. Colourless gas evolved; renders lime water turbid and also burns with a blue flame; no blackening.	CO and $\text{CO}_2$ from <i>oxalate</i> .
9. Yellow coloration in cold: upon warming, vigorous reaction, COS (burns with blue flame), $\text{SO}_2$ (decolourises fuchsin solution) and free S produced.	COS, $\text{SO}_2$ and S from <i>thiocyanate</i> .

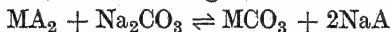
#### V, 4. EXAMINATION FOR ACID RADICALS (ANIONS) IN SOLUTION

The preliminary tests (vii) and (viii) with dilute sulphuric acid and with concentrated sulphuric acid will have provided useful information as to many acid radicals present. For more detailed information, it is necessary to have a solution containing all (or most) anions free from heavy metals. This is best prepared by boiling the substance with concentrated sodium carbonate solution; double decomposition occurs (either partially or completely) with the production of the insoluble carbonates\* of the metals (other than alkali metals) and the soluble sodium salts of the anions, which pass into solution.

\* Certain carbonates, initially formed, are converted into insoluble basic carbonates or into hydroxides.



Thus, if the unknown substance is the salt of a bivalent metal M and an acid HA, the following reaction will occur:



The carbonate  $\text{MCO}_3$  is insoluble and the sodium salt NaA will pass into solution whether  $\text{MA}_2$  is soluble in water or not.

**Preparation of solution for testing for anions.**—Boil 1 gram of the finely divided substance or mixture with 25 ml. of a saturated solution of pure sodium carbonate\* (prepared from 4 grams of anhydrous sodium carbonate and 25 ml. of distilled water) for 10 minutes in a small conical flask with a funnel in the mouth to reduce the loss by evaporation. Filter,† wash the residue with hot distilled water and collect the washings together with the main filtrate; the total volume should be 30–35 ml. Reject the residue. The sodium carbonate extract will be termed the “ $\text{Na}_2\text{CO}_3$  prepared solution.” Use this solution to carry out the following tests.

**1. Sulphate test.**—To 2 ml. of the “ $\text{Na}_2\text{CO}_3$  prepared solution” add dilute hydrochloric acid until acid (test with litmus paper) and then add 2 ml. in excess. Boil for 1–2 minutes to expel carbon dioxide completely, and then add about 1 ml. of barium chloride solution. A white precipitate ( $\text{BaSO}_4$ ) shows the presence of *sulphate*. Confirm by test 1 in Section IV, 24 (charcoal reduction of precipitate).

**2. Test for reducing agents.**—Acidify 2 ml. of the “ $\text{Na}_2\text{CO}_3$  prepared solution” with dilute sulphuric acid and add 1 ml. of dilute sulphuric acid in excess. Add 3–4 drops of 0.02N potassium permanganate solution (prepared by diluting 1 ml. of 0.1N  $\text{KMnO}_4$  to 5 ml.) from a dropper. Bleaching of the permanganate indicates the presence of one or more of the following reducing anions: *sulphite, thiosulphate, sulphide, nitrite, bromide, iodide and arsenite*. If the permanganate is not decolourised, heat and observe the result. If the reagent is bleached only on heating, the presence of *oxalate* is indicated. A negative test shows the absence of the above anions.

**3. Test for oxidising agents.**—Treat 2 ml. of the “ $\text{Na}_2\text{CO}_3$  prepared solution” cautiously with 1 ml. of concentrated hydrochloric acid, followed by 2 ml. of the manganous chloride

\* It is essential to use pure sodium carbonate; the A.R. solid is satisfactory. Some “pure” samples may contain traces of sulphate or chloride: the absence of these impurities should be confirmed by a blank experiment.

† If no precipitate is obtained, the substance is free from heavy metals, and the sodium carbonate treatment may be omitted if more of the solution is required.

reagent. A brown (or black) coloration indicates the presence of *nitrate*, *nitrite*, *chlorate* or *chromate*. A negative test indicates the absence of the above oxidising anions except small amounts of nitrates and nitrites. If reducing anions have been found, this test is inconclusive.

*Note.*—The reagent consists of a saturated solution of manganous chloride,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ , in concentrated hydrochloric acid. Its action depends upon its conversion by even mild oxidising agents to a dark-brown coloured manganic salt, probably containing the complex  $[\text{MnCl}_6]^{--}$  or  $[\text{MnCl}_4]^-$  ions.

**4. Tests with silver nitrate solution.**—Sulphide and sulphite interfere in the tests with silver nitrate solution, hence if either of these anions was detected in the preliminary test with dilute sulphuric acid, it must be removed first as follows. Acidify 10 ml. of the " $\text{Na}_2\text{CO}_3$  prepared solution" with dilute acetic acid (use litmus paper): boil gently in a conical flask or porcelain dish in the fume cupboard to expel hydrogen sulphide or sulphur dioxide (3–5 minutes). It is important that the solution be acid throughout. Filter, if necessary, and allow to cool. If the volume has been reduced appreciably, add water to restore the original volume (solution S).

Acidify 10 ml. of the " $\text{Na}_2\text{CO}_3$  prepared solution" cautiously with dilute acetic acid (use litmus paper). Determine the volume of the acidified solution (or of solution S) with the aid of a small measuring cylinder, add one-tenth of the volume of concentrated  $\text{HNO}_3$  and stir for 30 seconds. Then add  $\text{AgNO}_3$  solution with stirring until precipitation is complete. Heat to the boiling point, allow the precipitate to settle, cool and filter. Wash the precipitate with 2–3 ml. of *N* nitric acid.

**Residue.**  
 $\text{AgCl}$ —white.  
 $\text{AgBr}$ —pale yellow.  
 $\text{AgI}$ —yellow.

**Filtrate.** Add 1 ml. of  $\text{AgNO}_3$  solution, then 20%  $\text{NaNO}_2$  solution (prepared from the A.R. solid) dropwise and with stirring until precipitation is complete. [If no precipitate forms, do not add more than 0.5 ml. of  $\text{NaNO}_2$  solution.] Filter, if necessary, and wash with 2–3 ml. of *N* nitric acid.

**Residue.**  
 $\text{AgCl}$   
 derived from  
 $\text{AgClO}_3$ .

**Filtrate.** Add  $\text{NaOH}$  solution dropwise (use a dropper) and with vigorous stirring until neutral to litmus (1), then add 0.5 ml. of dilute acetic acid, followed by 1 ml. of  $\text{AgNO}_3$  solution, and heat to about  $80^\circ\text{C}$  (2). If a permanent precipitate forms, add more  $\text{AgNO}_3$  solution until precipitation is complete. Filter and wash with hot water.

**Residue (3).**  
 $\text{Ag}_3\text{PO}_4$ —yellow.  
 $\text{Ag}_3\text{AsO}_4$ —brownish-red.  
 $\text{Ag}_3\text{AsO}_3$ —yellow.  
 $\text{Ag}_2\text{C}_2\text{O}_4$ —white.

**Filtrate.**  
 Discard.

*Notes.* (1) It is essential that the solution be just neutral to litmus or, at most, barely alkaline: the latter will be indicated by a very slight brown opalescence (due to  $\text{Ag}_2\text{O}$ ) obtained upon stirring or shaking. If much silver oxide separates, it will re-dissolve only with difficulty.

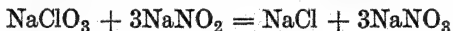
(2) Silver acetate is soluble in hot water and is held in solution.

(3) If chromate is present (yellow or orange solution), it will be reduced by the  $\text{NaNO}_2$  treatment and will precipitate here as green chromic hydroxide. *Chromate* is readily detected in the " $\text{Na}_2\text{CO}_3$  prepared solution" as follows: acidify (say, 2 ml.) with dilute  $\text{HNO}_3$ , cool, add 1 ml. of amyl alcohol and 0.5 ml. of 3 per cent  $\text{H}_2\text{O}_2$  solution and stir. A blue coloration ("*perchromic acid*") in the organic layer confirms chromate.

The separations described in the above table are based upon the following facts:

(i)  $\text{AgNO}_3$  solution precipitates only  $\text{AgCl}$ ,  $\text{AgBr}$  and  $\text{AgI}$  from a dilute nitric acid solution, the other silver salts being soluble.

(ii)  $\text{NaNO}_2$  solution reduces chlorate to chloride, which is precipitated as  $\text{AgCl}$  in the presence of  $\text{AgNO}_3$  solution:



(iii) In solutions faintly acid with acetic acid, phosphate, arsenate, arsenite and oxalate are precipitated by  $\text{AgNO}_3$  solution.

If a mixture of the halides, or of phosphate, arsenate or arsenite, is suspected, use Table *A* or Table *C* given in Section VII, 17. The confirmatory tests for individual anions are collected in Section V, 5. The reactions with silver nitrate solution are intended to act as a guide to the presence of groups of anions, and the table must be interpreted in conjunction with the observations made in the preliminary tests. Arsenite, arsenate and chromate will also be found in the analysis for cations (Section V, 7).

**5. Test with calcium chloride solution.\*** For tests 5 and 6 a " $\text{Na}_2\text{CO}_3$  practically neutral solution" is required. This is obtained as follows. Transfer 4-5 ml. of the " $\text{Na}_2\text{CO}_3$  prepared solution" to a porcelain dish and render it faintly acid with dilute nitric acid (use litmus paper). Boil for 3-4 minutes to expel carbon dioxide, allow to cool, then add dilute ammonia solution until just alkaline†; boil gently for 1 minute to remove any appreciable excess

\* Tests 5 and 6 may be omitted by those requiring only a beginner's course in qualitative analysis.

† If a ppt. forms on neutralising the solution, the presence of arsenic, antimony and tin sulphides and possibly salts of amphoteric bases (lead, tin, aluminium and zinc) is indicated. The ppt. should be filtered off and rejected.

of ammonia. Divide the solution into two equal parts; reserve half for test 6.

Add  $\text{CaCl}_2$  solution (equal in volume to that of the solution) and a little dilute acetic acid and allow to stand. A white precipitate indicates the presence of *oxalate* and/or *fluoride*. Filter off the precipitate and dissolve it by pouring a little hot dilute sulphuric acid into the filter. Treat the hot filtrate with a few drops of potassium permanganate solution. If the permanganate is reduced, *oxalate* is present.

**6. Test with ferric chloride solution.\*** Treat the other portion of the "neutral" solution from test 5 with aqueous  $\text{FeCl}_3$  solution.

Reddish-purple coloration indicates *thiosulphate*.

Reddish-brown coloration, yielding a brown precipitate on dilution and boiling, indicates *acetate*.

Yellowish-white precipitate indicates *phosphate*.

Blood-red coloration, discharged by  $\text{HgCl}_2$  solution, indicates *thiocyanate*.

## V, 5. CONFIRMATORY TESTS FOR ACID RADICALS (ANIONS)

The tests in the preceding section will indicate the acid radicals or anions present. In general, these should be confirmed by at least one distinctive confirmatory test. The following are recommended. Full experimental details will usually be found in Chapter IV under the reactions of the acid radicals (anions); the reference to these will be abbreviated as follows: thus (IV, 2, 7) is to be interpreted as Section IV, 2, reaction 7. It is assumed, of course, that interfering acids are absent or have been removed as described below under *Special Tests for Mixtures of Acid Radicals*.

**Chloride.** Heat solid with concentrated  $\text{H}_2\text{SO}_4$  and  $\text{MnO}_2$ ;  $\text{Cl}_2$  evolved (reddens then bleaches litmus paper and also turns KI-starch paper blue) (IV, 14, 2).

**Bromide.** Heat solid with concentrated  $\text{H}_2\text{SO}_4$  and  $\text{MnO}_2$ ;  $\text{Br}_2$  evolved (IV, 15, 2) OR chlorine water (or the equivalent  $\text{NaOCl}$  solution and dilute  $\text{HCl}$ ) and  $\text{CCl}_4$  test; reddish-brown coloration of  $\text{CCl}_4$  layer (IV, 15, 5).

**Iodide.** Chlorine water (or  $\text{NaOCl}$  solution and dilute  $\text{HCl}$ ) and  $\text{CCl}_4$  test; violet coloration of  $\text{CCl}_4$  layer (IV, 16, 4).

\* The bench reagent usually contains excess of free acid added during its preparation in order to produce a clear solution: this may prevent the precipitation of the basic acetate on boiling. It is therefore recommended that dilute  $\text{NH}_3$  solution be added dropwise to the side-shelf  $\text{FeCl}_3$  solution until a slight permanent precipitate forms; the precipitate is filtered off. The filtrate may be termed "neutral  $\text{FeCl}_3$  solution."

**Fluoride.** Silicon tetrafluoride test (heat with concentrated  $\text{H}_2\text{SO}_4$  in a test-tube) (IV, 17, 1); test 8 in VII, 16; zirconium-alizarin-S test (IV, 17, 6).

**Nitrite.** Brown ring test with dilute acetic acid or with dilute  $\text{H}_2\text{SO}_4$  (IV, 7, 2) OR thiourea test (IV, 7, 9).

**Nitrate.** Brown ring test with concentrated  $\text{H}_2\text{SO}_4$  (IV, 18, 3), if bromide, iodide and nitrite absent.

**Sulphide.** Dilute  $\text{H}_2\text{SO}_4$  on solid, and action of  $\text{H}_2\text{S}$  on lead or cadmium acetate paper (IV, 6, 1).

**Sulphite.** Dilute  $\text{H}_2\text{SO}_4$  on solid, odour of  $\text{SO}_2$  and action of  $\text{SO}_2$  on  $\text{K}_2\text{Cr}_2\text{O}_7$  paper (IV, 4, 1), or upon fuchsin solution (IV, 4, 10);  $\text{BaCl}_2$ - $\text{Br}_2$  water test (IV, 4, 2).

**Thiosulphate.** Dilute  $\text{H}_2\text{SO}_4$  on solid and liberation of  $\text{SO}_2$  ( $\text{K}_2\text{Cr}_2\text{O}_7$  paper test or fuchsin solution test) and sulphur (IV, 5, 1).

**Sulphate.** The  $\text{BaCl}_2$  solution and dilute  $\text{HCl}$  test is fairly conclusive. Further confirmation is obtained by reduction of the ppt. ( $\text{BaSO}_4$ ) on charcoal to sulphide (test for latter with lead acetate solution) (IV, 24, 1).

**Carbonate.** Action of dilute  $\text{H}_2\text{SO}_4$  on solid, and lime water test (IV, 2, 1).

**Hypochlorite.** Action of dilute  $\text{HCl}$  and test for  $\text{Cl}_2$  evolved (IV, 13, 4).

**Chlorate.** The  $\text{AgNO}_3$ - $\text{NaNO}_2$  test (IV, 19, 3).

**Chromate.** Hydrogen peroxide test with amyl alcohol as organic solvent (IV, 33, 4).

**Arsenite.** Immediate ppt. of  $\text{As}_2\text{S}_3$  in dilute  $\text{HCl}$  solution (III, 11, 1) and absence of ppt. with  $\text{Mg}(\text{NO}_3)_2$  reagent (III, 11, 3).

**Arsenate.** Action of  $\text{H}_2\text{S}$  on acid solution (III, 12, 1),  $\text{AgNO}_3$  solution test in faintly acetic acid solution (III, 12, 2) and  $\text{Mg}(\text{NO}_3)_2$  reagent test (III, 12, 3).

**Phosphate.** Ammonium molybdate test (temperature not above  $40^\circ$ ) (IV, 28, 4).

**Cyanide.** Prussian blue test (IV, 8, 4) or ammonium sulphide test (IV, 8, 16).

**Thiocyanate.** Ferric chloride solution test: colour discharged by  $\text{HgCl}_2$  solution or by  $\text{NaF}$  solution, but not by  $\text{HCl}$  (IV, 10, 6).

**Acetate.** Action of ethyl or of *n*-butyl alcohol and concentrated  $\text{H}_2\text{SO}_4$  (IV, 35, 3) OR indigo test (IV, 35, 9) using ordinary test-tube or ignition tube.

**Oxalate.** The  $\text{CaCl}_2$  test and decolourisation of acidified  $\text{KMnO}_4$  solution at about  $70^\circ$  is sufficiently conclusive.

## V, 6. SPECIAL TESTS FOR MIXTURES OF ACID RADICALS\*

**1. Carbonate in the presence of Sulphite.**—Sulphites, on treatment with dilute sulphuric acid, liberate sulphur dioxide which, like carbon dioxide, produces a turbidity with lime or baryta water. The dichromate test for sulphites is, however, not influenced by the presence of carbonates. To detect carbonates in the presence of sulphites, treat the solid mixture with dilute sulphuric acid and pass the evolved gases through a small wash-bottle or boiling tube containing potassium dichromate solution and dilute sulphuric acid. The solution will be turned green and the sulphur dioxide will, at the same time, be completely removed; the residual gas is then tested with lime water in the usual manner.

An alternative procedure is to add a little powdered potassium dichromate to the mixture and then to warm with dilute sulphuric acid: the evolved gas is then passed through lime water.

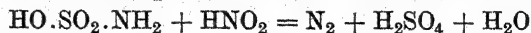
The above method can, of course, be applied in the presence of thiosulphates.

**2. Nitrate in the presence of Nitrite.**—The nitrite is readily identified in the presence of a nitrate by treatment with dilute mineral acid, potassium iodide and starch paste (or potassium iodide-starch paper) or by means of the thiourea test. The nitrate cannot, however, be detected in the presence of nitrite since the latter gives the brown ring test with ferrous sulphate solution and *dilute* sulphuric acid. The nitrite is therefore completely decomposed first by one of the following methods:

(i) boil with ammonium chloride solution until effervescence ceases;†

(ii) warm with urea and dilute sulphuric acid until evolution of gas ceases;†

(iii) add a little sulphamic acid to the solution:



The last-named is probably the simplest and most efficient method for the removal of nitrite in aqueous solution.

The brown ring test for nitrate can then be applied.

**3. Nitrate in the presence of Bromide and Iodide.**—The brown ring test for nitrates cannot be applied in the

\* Full experimental details of the various tests will be found in Chapter IV.

† Traces of nitrate are always formed in this reaction.

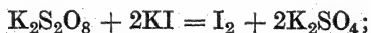
presence of bromides and iodides since the liberation of free halogen with concentrated sulphuric acid will obscure the brown ring due to the nitrate. The solution is therefore boiled with sodium hydroxide solution until ammonium salts, if present, are completely decomposed, and the solution is then cooled under the tap. Powdered Devarda's alloy or aluminium powder or zinc dust is then added and the mixture *gently* warmed. The evolution of ammonia, detected by its smell, its action upon red litmus paper and upon mercurous nitrate paper (see Section III, 36, reaction 1) indicates the presence of a nitrate.

An alternative method is to remove the halides by precipitation with an almost saturated solution of silver sulphate (nitrate-free) and any excess of the latter with sodium carbonate solution; the nitrate is then tested for in the filtrate in the usual way (see also Section IV, 45, 4).

**4. Nitrate in the presence of Chlorate.**—The chlorate interferes with the brown ring test (compare Section IV, 19, reaction 1). The nitrate is reduced to ammonia as described under 3; the chlorate is at the same time reduced to chloride which may be tested for with silver nitrate solution and dilute nitric acid.

If a chloride is originally present, it may be removed first by the addition of saturated silver sulphate solution.

**5. Chloride in the presence of Bromide and Iodide.**—This procedure involves the removal of the bromide and iodide with potassium or ammonium persulphate in the presence of dilute sulphuric acid. The free halogens are thus liberated, and may be eliminated either by simple evaporation (addition of water may be necessary to maintain the original volume) or by evaporation at about 80° in a stream of air.



Add solid potassium or ammonium persulphate to the "Na<sub>2</sub>CO<sub>3</sub> prepared solution" of the mixed halides contained in a conical flask; strongly acidify with dilute sulphuric acid; heat the flask to about 80°, and aspirate a current of air through the solution with the aid of a filter pump (see Fig. IV, 45, 1 in Section IV, 45, 5) until the solution is colourless. Add more solid persulphate or water as may be found necessary. Test the residual colourless liquid for chloride with silver nitrate solution and dilute nitric acid.

**6. Chloride in the presence of Iodide (Bromide being absent).**—Acidify the “ $\text{Na}_2\text{CO}_3$  prepared solution” with dilute nitric acid, add excess of silver nitrate solution, and filter; reject the filtrate. Wash the precipitate with dilute ammonia solution and collect the washings. Add dilute nitric acid to the washings; a white precipitate of silver chloride indicates the presence of chloride.

The separation is based upon the solubility of silver chloride in dilute ammonia solution and the practical insolubility of silver iodide in this reagent.

**7. Chloride in the presence of Bromide (Iodide being absent).**—Acidify the “ $\text{Na}_2\text{CO}_3$  prepared solution” with dilute nitric acid and add an equal volume of concentrated nitric acid. Boil for 5 minutes or until all the bromine is expelled; then add silver nitrate solution. A white precipitate indicates chloride present.

**8. Bromide and Iodide in the presence of one another.**—The presence of a chloride does not interfere with the reactions described below. Acidify the “ $\text{Na}_2\text{CO}_3$  prepared solution” with dilute sulphuric acid and add 1–2 ml. of carbon tetrachloride; add 1–2 drops of dilute sodium hypochlorite solution\* (best with a dropper), and shake; a violet coloration in the carbon tetrachloride layer indicates iodide. Continue the addition of the hypochlorite solution *drop by drop* to oxidise the iodine to iodate (colourless) and shake after each addition. The violet colour will disappear, and a reddish-brown coloration of the carbon tetrachloride layer, due to dissolved bromine (or to bromine chloride  $\text{BrCl}$ ), will be obtained if a bromide is present. If iodide alone is present, the solution will be colourless after the violet colour has disappeared.

**9. Phosphate in the presence of Arsenate.**—Both arsenate and phosphate give a yellow precipitate on warming with ammonium molybdate solution and nitric acid, the latter on gentle warming (not above  $40^\circ$ ) and the former on boiling. Also both anions give a white precipitate with the magnesium nitrate reagent (or with magnesia mixture). It must also be remembered in connexion with the precipitation of Group II

\* The use of dilute sodium hypochlorite solution and dilute acid is far more satisfactory than chlorine water. Alternatively, a solution of chloramine-T (15 grams per litre) may be employed; this is a source of hypochlorous acid (and therefore of chlorine):

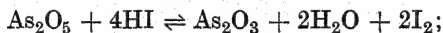




that arsenates are only slowly precipitated by hydrogen sulphide in dilute acid solution.

Acidify the " $\text{Na}_2\text{CO}_3$  prepared solution" with dilute hydrochloric acid, pass in sulphur dioxide to reduce the arsenate to arsenite, boil off the excess of sulphur dioxide (test with potassium dichromate paper), and pass hydrogen sulphide into the solution to precipitate the arsenic as arsenious sulphide: continue the passage of hydrogen sulphide until no more precipitate forms. Filter, boil off the hydrogen sulphide and test the filtrate for phosphate by the ammonium molybdate test or with the magnesium nitrate reagent.

An alternative method for the elimination of arsenate is the following. Acidify the " $\text{Na}_2\text{CO}_3$  prepared solution" with dilute hydrochloric acid and then add one-quarter of the volume of concentrated hydrochloric acid (the total volume should be about 10 ml.). Add 0.5 ml. of 5 per cent ammonium iodide solution, heat to boiling and pass hydrogen sulphide into the boiling solution until precipitation is complete (5–10 minutes). Filter off the arsenious sulphide, and boil off the hydrogen sulphide from the filtrate. Add dilute ammonia solution until alkaline and excess of the magnesium nitrate reagent (or of magnesia mixture). A white precipitate indicates the presence of phosphate.



If the white precipitate of magnesium ammonium phosphate be washed with a little water, and then treated on the filter with a little silver nitrate solution containing a few drops of dilute acetic acid, a yellow coloration, due to silver phosphate, is obtained. However, a similar reaction with the white precipitate produced by the magnesium nitrate reagent with a mixture of phosphate and arsenate (*i.e.*  $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O} + \text{Mg}(\text{NH}_4)\text{AsO}_4 \cdot 6\text{H}_2\text{O}$ ) yields a brownish-red coloration on the white precipitate; this is due to silver arsenate.

It may be pointed out that if arsenite is also present, it may be readily detected in the filtrate obtained by treating the original mixture of arsenate, phosphate and arsenite with the magnesium nitrate reagent: upon acidifying with *N* hydrochloric acid and passing hydrogen sulphide, an immediate yellow precipitate of arsenious sulphide is produced.

## V, 7. EXAMINATION FOR METAL IONS (CATIONS) IN SOLUTION

**Preparation of a solution of the solid.**—Since the whole scheme for the analysis of cations depends upon the reactions of ions, it is clear that it is first necessary to get the substance into solution. Water is first tried in the cold and then on warming. If insoluble in water, the following reagents are investigated as solvents in the order indicated: dilute hydrochloric acid, concentrated hydrochloric acid, dilute nitric acid, concentrated nitric acid, and aqua regia (3 volumes of concentrated HCl to 1 volume of concentrated  $\text{HNO}_3$ ). Most substances encountered in an elementary course will dissolve in either water or dilute hydrochloric acid. If concentrated hydrochloric acid has to be used, the solution must be considerably diluted (to 0.3*N*) before proceeding with the analysis, otherwise certain cations, such as cadmium and lead, will not be precipitated by hydrogen sulphide. When concentrated nitric acid or aqua regia is employed as the solvent, the solution must be evaporated almost to dryness, a little hydrochloric acid added, the solution evaporated again to small bulk, and then diluted with water to dissolve the soluble nitrates (or chlorides). This evaporation is necessary because the nitric acid may react with the hydrogen sulphide subsequently employed in the Group analysis.

To discover the most suitable solvent, treat portions of 0.2 gram\* of the finely powdered substance successively with 3–4 ml. of (1) water, (2) dilute hydrochloric acid, (3) concentrated hydrochloric acid, (4) dilute nitric acid, (5) concentrated nitric acid and (6) aqua regia in the order given. Try the solubility first in the cold and then on warming; if in doubt whether the substance or a portion of the substance has dissolved, evaporate a little of the clear solution on a watch glass. If the substance dissolves in water, proceed immediately to the test for the metal ions. If the use of dilute hydrochloric acid results in the formation of a precipitate, this may consist of the metals of Group I; the precipitate may either be filtered off and examined for this Group, or else the original substance may be dissolved in dilute nitric acid. If concentrated acids are employed for dissolution, the remarks in the previous paragraph must be borne in mind.

When a suitable solvent has been found, the solution for

\* This is most simply estimated by weighing out 1 gram and dividing it into 5 approximately equal parts.

analysis is prepared with about 0.5 gram of the solid: the volume of the final solution should not exceed 15 ml.

Before describing the general scheme for the separation of the cations into groups, the student should take note of the following facts:

(1) The analysis should not be conducted with large quantities of the substance because much time will be spent in filtering the precipitates and difficulty may be experienced in washing and dissolving them. It is therefore recommended that about 0.5 gram be employed for the analysis. After a little experience the student will be able to judge from the relative sizes of the precipitates the relative quantities of the various components present in the mixture.

(2) The tests must, in the first place, be carried out in the order given. A group reagent will separate its particular group from those which follow it and not from those which precede it. Thus hydrogen sulphide in the presence of 0.3*N* hydrochloric acid will separate Group II from Groups IIIA, IIIB, IV and V, but does not separate Group II from Group I. It is most important, therefore, that one group should be completely precipitated before precipitation of the next group is attempted, otherwise the group precipitate will be contaminated by metals from the preceding groups and misleading results will be obtained.

### **Oxides, Hydroxides, Free Metals and Simple Alloys.—**

If a solid substance is found to contain no anions, it may be an oxide, or hydroxide, or a metal or a mixture of metals, or an alloy. Metals and alloys have certain characteristic physical properties; many metals evolve hydrogen on treatment with dilute acids. As a rule, nitric acid must be employed as solvent, and it will then be necessary to remove the excess of nitric acid (as already described above) before proceeding to the group analysis.

Table S below contains full details for the separation of the cations into the individual groups: the *Notes* following the Table contain much useful information and should be read before the separation into groups is attempted. The references to individual Group Separation Tables are to those already given in Chapter III.

#### **NOTES ON TABLE S (SIMPLIFIED GENERAL TABLE FOR SEPARATION OF CATIONS INTO GROUPS)**

This Table and the Notes which follow are intended for beginners and in consequence the various operations are given in somewhat greater detail than in Table I (Section VII, 6).

## 7, 8.

## Table S.—Separation of Cations into Groups

(Organic Acids, Boric, Hydrofluoric, Silicic and Phosphoric Acids being absent)

Add a few drops of dilute HCl to the cold solution. If a ppt. forms, continue adding dilute HCl until no further precipitation takes place. Filter (1) and wash the ppt. with a little water; add washings to filtrate (2).	
<b>Residue.</b> The ppt. may contain: PbCl <sub>2</sub> —white. Hg <sub>2</sub> Cl <sub>2</sub> —white. AgCl—white. <b>Group I (Silver Group) present.</b> Examine by Group Separation Table I (Section III, 5).	<b>Filtrate.</b> This must give no further precipitate with a few drops of dilute HCl. Add 1 ml. of 3% H <sub>2</sub> O <sub>2</sub> solution (3). Adjust the HCl concentration to 0.3N (4). Heat to boiling and pass H <sub>2</sub> S through the solution until precipitation is complete (5). Filter and wash (6).
<b>Residue.</b> The ppt. may contain: PbS—black. PbS <sub>2</sub> —black. Bi <sub>2</sub> S <sub>3</sub> —black or dark brown. CdS—yellow. SnS—black. SnS <sub>2</sub> —yellow. Sb <sub>2</sub> S <sub>3</sub> —orange. As <sub>2</sub> S <sub>3</sub> —yellow. <b>Groups IIA and IIB (Copper and Arsenic Groups) present.</b> Examine by Group Separation Tables II and III or IIA (Section III, 10 and III, 18).	<b>Filtrate.</b> Test a small portion with H <sub>2</sub> S to be certain that precipitation of Group II is complete. Boil down to about 10 ml. in a porcelain dish and thus ensure that all H <sub>2</sub> S has been removed (test with lead acetate paper). Add 1–2 ml. of concentrated HNO <sub>3</sub> and boil to oxidize any ferrous salt to the ferric state (7). Add 1–2 grams of solid NH <sub>4</sub> Cl, heat to boiling, add dilute NH <sub>3</sub> solution until mixture is alkaline and then 1 ml. in excess, boil for 1 minute and filter immediately. Wash (8).
<b>Residue.</b> The ppt. may contain: Fe(OH) <sub>3</sub> —red-dish brown. Cr(OH) <sub>3</sub> —green. Al(OH) <sub>3</sub> —white. MnO <sub>2</sub> ·xH <sub>2</sub> O—brown. <b>Group IIIA (Iron Group) present.</b> Examine by Group Separation Table IV (Section III, 23).	<b>Filtrate.</b> Add 2–3 ml. of dilute NH <sub>3</sub> solution, heat, pass H <sub>2</sub> S (under "pressure") for 1 minute. Filter (9) and wash (10).
<b>Residue.</b> The ppt. may contain: CoS—black. NiS—black. MnS—pink. ZnS—white. <b>Group IIIB (Zinc Group) present.</b> Examine by Group Separation Table V (Section III, 28).	<b>Filtrate.</b> This must give no further ppt. with H <sub>2</sub> S (9). Transfer to a porcelain dish and acidify with dilute acetic acid (11). Evaporate to a pasty mass [FUME CUPBOARD], allow to cool, add 2–3 ml. of concentrated HNO <sub>3</sub> so as to wash the solid around the walls to the centre of the dish and heat cautiously until the mixture is dry. Then heat more strongly until no more white fumes are evolved (12). Cool. Add 3 ml. of dilute HCl and 10 ml. of water: warm and stir to dissolve the salts. Filter, if necessary. Add 0.25 gram of solid NH <sub>4</sub> Cl (or 2.5 ml. of 10% NH <sub>4</sub> Cl solution), render alkaline with concentrated NH <sub>3</sub> solution and then add, with stirring, (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> solution in slight excess. Keep and stir, the mixture in a water bath at 50–60°C for 3–5 minutes (13). Filter and wash with a little hot water.
<b>Residue.</b> The ppt. may contain: BaCO <sub>3</sub> —white. SrCO <sub>3</sub> —white. CaCO <sub>3</sub> —white. <b>Group IV (Calcium Group) present.</b> Examine by Group Separation Table VI (Section III, 32).	<b>Filtrate.</b> May contain Mg <sup>++</sup> , Na <sup>+</sup> and K <sup>+</sup> (14). Evaporate to a pasty mass in a porcelain dish [FUME CUPBOARD], add 2 ml. of concentrated HNO <sub>3</sub> , evaporate cautiously to dryness and then heat until white fumes cease to be evolved. White residue. <b>Group V (Alkali Group) present.</b> Examine by Group Separation Table VII (Section III, 37).

Note. In Group Separation Tables I, II, IIA, IV, V and VI, commence at the point marked (T).

(1) If the substance was completely soluble in dilute HCl, it is evident that no silver or mercurous salt is present. When lead is present, the solution may be clear while hot, but  $\text{PbCl}_2$  is deposited upon cooling the solution, due to the slight solubility of the salt in cold water. Lead may be found in Group II, even if it is not precipitated in Group I.

(2) It is usually advisable in group separations to wash a precipitate with a small volume of a suitable wash solution and to add the washings to the filtrate. In the present instance cold water or cold very dilute HCl (say, 0.5*N*) may be used. The precipitating reagent, diluted 10–100-fold, is generally a suitable wash liquid. Specific directions for washing precipitates will usually be omitted from the present Table in order to economise space.

(3) The  $\text{H}_2\text{O}_2$  solution is added to oxidise  $\text{Sn}^{++}$  to  $\text{Sn}^{++++}$ , thus leading ultimately to the precipitation of  $\text{SnS}_2$  instead of the somewhat gelatinous  $\text{SnS}$ . The excess of  $\text{H}_2\text{O}_2$  should be decomposed by boiling before passing  $\text{H}_2\text{S}$ , otherwise some S may be precipitated. The subsequent separation of Groups IIA and IIB by means of aqueous KOH is thus rendered more complete, since  $\text{SnS}_2$  dissolves entirely and  $\text{SnS}$  dissolves only partially in aqueous KOH.

If it is intended to use ammonium polysulphide in the separation of Groups IIA and IIB, the addition of  $\text{H}_2\text{O}_2$  is not essential since the  $(\text{NH}_4)_2\text{S}_x$  will oxidise the  $\text{SnS}$  to  $\text{SnS}_2$  and the latter dissolves as the thiostannate  $(\text{NH}_4)_2\text{SnS}_3$ .

(4) It is important that the concentration of the HCl be approximately correct, *i.e.* 0.3*M*, before passing  $\text{H}_2\text{S}$ : with higher concentrations of acid, lead, cadmium and stannous tin will be incompletely precipitated. If the acidity is too low, sulphides of Group IIIB ( $\text{NiS}$ ,  $\text{CoS}$  and  $\text{ZnS}$ ) may be precipitated.

Either of two methods may be employed to adjust the acid concentration.

(a) Concentrate the solution (if necessary) to a volume of 10–15 ml., cool. Add concentrated  $\text{NH}_3$  solution dropwise from a dropper (the commercial “medicine dropper” is satisfactory), with constant stirring, until the mixture is just alkaline. Introduce dilute HCl dropwise (use a dropper) until the mixture is just acid (use litmus paper). Then add 2.0 ml. of 3*N* HCl (measured from a graduated pipette or calibrated dropper) and dilute the solution to a volume of 20 ml. with distilled water.

(b) An alternative procedure is to make use of the indicator methyl violet (0.1 per cent aqueous solution or, better, the purchased or prepared indicator paper). The following table gives the colour of the indicator at various concentrations of acid:

<i>Acid concentration</i>	<i>pH</i>	<i>Methyl violet indicator</i>
Neutral or alkaline	7+	Violet.
0.1 <i>N</i> HCl	1.0	Blue.
0.25 <i>N</i> HCl	0.6	Blue-green.
0.33 <i>N</i> HCl	0.5	Yellow-green.
0.50 <i>N</i> HCl	0.3	Yellow.

Add 1 drop of methyl violet indicator solution and introduce dilute HCl or dilute  $\text{NH}_3$  solution (as necessary) dropwise and with constant stirring until the colour of the solution is yellow-green: a blue-green colour is almost but not quite acid enough, yet it is acceptable for most analyses. [If the indicator paper is available, the thoroughly stirred solution should be spotted on fresh portions of the paper.] It is recommended that a comparison solution containing, say, 10 ml. of 0.3*N* HCl and 1 drop of indicator be freshly prepared: this will facilitate the correct adjustment of the acidity. A more satisfactory standard is a buffer solution prepared by mixing 5 ml. of *N* sodium acetate and 10 ml. of *N* HCl: this has a pH of 0.5.

(5) For the passage of  $\text{H}_2\text{S}$  into the solution, the latter is placed in a small conical flask (one of 50 ml. capacity is suitable) or in a boiling tube and the "pressure" method used as detailed in Section II, 2, 7. Heat the solution almost to boiling and pass in  $\text{H}_2\text{S}$ , whilst slowly shaking the flask with a swirling motion, until precipitation is complete: the latter will be apparent when bubbling either stops altogether or is reduced to a very slow rate of 1-2 bubbles per minute. Saturation is normally reached in 2-5 minutes. The best method of determining whether precipitation is complete is to filter off a portion of the solution and test the filtrate with  $\text{H}_2\text{S}$ . If only a white precipitate or suspension of sulphur is obtained, the presence of an oxidising agent is indicated.

If an oxidising agent is present (e.g. a permanganate, dichromate or a ferric salt), as is shown by the gradual separation of a fine white precipitate of sulphur and/or a change in colour of the solution, it is usual to pass  $\text{SO}_2$  into the hot solution until reduction is complete, then to boil off the excess of  $\text{SO}_2$  (test with  $\text{K}_2\text{Cr}_2\text{O}_7$  paper), and finally to pass  $\text{H}_2\text{S}$ . Arsenates, in particular, are slowly precipitated by  $\text{H}_2\text{S}$ : they are therefore usually reduced by  $\text{SO}_2$  to arsenites and then precipitated as  $\text{As}_2\text{S}_3$  with  $\text{H}_2\text{S}$ , after prior removal of the excess of  $\text{SO}_2$  in order to avoid interaction of the latter with  $\text{H}_2\text{S}$  and the consequent separation of S. Stannic compounds may be very slightly reduced to the stannous state by this treatment; the amount of reduction is, however, so small that it may be neglected. The original solution or substance must be tested for the valence state of the arsenic.

The objection to the use of  $\text{SO}_2$  is that some sulphuric acid may be formed, especially upon boiling, and this may partially precipitate Pb, Sr and Ba as sulphates. Any precipitate formed in this process should accordingly be examined for these cations:  $\text{PbSO}_4$  is soluble in ammonium acetate solution.

An alternative procedure to be borne in mind when arsenate, etc., is present, which does not possess the disadvantages associated with  $\text{SO}_2$  and is perhaps more expeditious, is to add 2-3 ml. of concentrated HCl and 0.5 ml. of 10 per cent  $\text{NH}_4\text{I}$  solution. The arsenate is thereby reduced to arsenite and upon saturation of the

hot solution with  $\text{H}_2\text{S}$  under "pressure," the arsenic is completely precipitated as  $\text{As}_2\text{S}_3$ . This reduction can be carried out after the sulphides of the other elements have been precipitated in the presence of 0.3N HCl.

(6) The wash liquid is prepared by dissolving 0.5 gram of  $\text{NH}_4\text{NO}_3$  in 10 ml. of water and treating this solution with  $\text{H}_2\text{S}$ ; about 5 ml. will suffice for the washing. The  $\text{H}_2\text{S}$  must be present in the wash liquid to prevent oxidation of some of the moist sulphides to sulphates.

(7) If the iron was originally present in the ferric state, it will be reduced to the ferrous condition by  $\text{H}_2\text{S}$ . It must be oxidised to the ferric state (1-2 ml. of saturated  $\text{Br}_2$  water may also be used) in order to ensure complete precipitation with  $\text{NH}_4\text{Cl}$  and dilute  $\text{NH}_3$  solution. The original solution must be tested to determine whether the iron is present as  $\text{Fe}^{++}$  or as  $\text{Fe}^{+++}$ .

(8) The washing may be made with a little hot water or, better, with 2 per cent  $\text{NH}_4\text{NO}_3$  solution.

(9) If the filtrate is brown or dark-coloured, Ni may be suspected. The dark-coloured solution contains colloidal  $\text{NiS}$ , which runs through the filter paper. It may be acidified with acetic acid and boiled until the  $\text{NiS}$  is coagulated: this may either be added to the Group IIIB precipitate or tested separately for Ni. As a general rule the addition of macerated filter paper (*e.g.* in the form of a portion of a Whatman filtration accelerator or ashless tablet) to the suspension before filtration will lead to a clear or colourless filtrate.

(10) The wash liquid may consist of 1 per cent  $\text{NH}_4\text{Cl}$  solution containing 1 per cent by volume of ammonium sulphide solution. Oxidation of the moist sulphides to soluble sulphates is thus considerably minimised.

(11) The filtrate must be immediately acidified and concentrated to remove  $\text{H}_2\text{S}$ . Ammonium sulphide solution on exposure to air slowly oxidises to ammonium sulphate and would then precipitate any barium or strontium present as  $\text{BaSO}_4$  and  $\text{SrSO}_4$ . Another reason for acidifying the filtrate from Group IIIB is to prevent the absorption of  $\text{CO}_2$  from the air with the formation of carbonate ions; the latter would also precipitate the ions of Group IV.

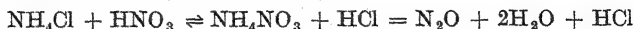
(12) The initial filtrate from Group IIIB will be almost saturated with ammonium salts. This concentration of ammonium ions is higher than is necessary to prevent the precipitation of  $\text{Mg}(\text{OH})_2$  and it may also lead to incomplete precipitation of the carbonates of Group IV metals. The latter effect is due to the acidic properties of ammonium ion:



the concentration of  $\text{CO}_3^{--}$  ions upon the addition of  $(\text{NH}_4)_2\text{CO}_3$  would thus be considerably decreased, and incomplete precipitation

of Group IV may occur. For these reasons most of the ammonium salts must be eliminated first.

Concentrated  $\text{HNO}_3$  decomposes  $\text{NH}_4\text{Cl}$  at a lower temperature than is required for its volatilisation:



Loss by decrepitation and spirting during this operation must be avoided.

(13) Ammonium carbonate decomposes appreciably above  $60^\circ\text{C}$ :



The digestion also improves the filtering properties of the precipitate.

(14) Owing to the slight solubility of  $\text{CaCO}_3$ ,  $\text{SrCO}_3$  and  $\text{BaCO}_3$  in solutions of ammonium salts, the filtrate from Group IV will, when these metals are present, contain minute amounts of the ions of the alkaline earth metals. Since the Group IV metals may interfere to a limited extent with the flame tests for Na and K and also the  $\text{Na}_2\text{HPO}_4$  test for Mg (if employed), it has been recommended that the filtrate from Group IV be heated with a little (say, 1 ml.) of  $(\text{NH}_4)_2\text{SO}_4$  solution and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution and filtered from any precipitate which forms. Owing to the comparatively small concentration of ammonium salts, this is generally unnecessary if the procedure described in Table VII (Section III, 37) is adopted.

**V, 9. Modification of the analysis in the presence of phosphate.**—Certain anions, which include phosphate, fluoride, borate, silicate and also those derived from organic acids such as acetate and oxalate, interfere with the cation analysis after Group II. Thus the presence of phosphate, fluoride, borate or oxalate ions will cause the metals of Groups IIIB and IV and also Mg to precipitate when the solution is made ammoniacal in Group IIIA. The various interfering anions and their removal or elimination are discussed in detail in Chapters VII and VIII. It is unlikely that the student will encounter any of the interfering anions in elementary analysis with the possible exception of phosphate. The manner of removal of phosphate is therefore given in the following table (Table P) as an illustration of the procedure to be adopted in dealing with an important interfering anion. The student will appreciate that the phosphate separation need not be made even if  $\text{PO}_4^{---}$  has been shown to be present (*e.g.* by the ammonium molybdate test) if no precipitate is obtained in Group IIIA. (with  $\text{NH}_4\text{Cl}$  and aqueous  $\text{NH}_3$ ) and also when it is known that Group IV and Mg are absent.



## V, 9. Table P.—Phosphate Separation Table

Boil the filtrate from Group II until free from  $\text{H}_2\text{S}$ , add a few drops of concentrated  $\text{HNO}_3$  (or 1–2 ml. of bromine water) and boil gently for 1 minute. Test a small portion for phosphate with ammonium molybdate and nitric acid, and a further portion for the presence of Groups IIIA, IIIB, IV or Mg by the addition of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_3$  solution. If both tests are positive, proceed as follows.

Adjust the volume of the solution to 10 ml. (1). Add 0.5–1 gram of solid  $\text{NH}_4\text{Cl}$ , stir until dissolved, then add the zirconium nitrate reagent slowly and with stirring until precipitation is complete (2); a large excess of the reagent must be avoided. Heat the contents of the test-tube or small conical flask to boiling and stir with a glass rod to prevent bumping. Filter through a Whatman No. 32 filter paper (3): wash the ppt. with a little hot water and combine the washings with the filtrate.

<b>Residue.</b> Zirconium phosphate. Reject.	<b>Filtrate.</b> Test if all the phosphate has been precipitated by the addition of a drop of the zirconium nitrate reagent: if no ppt. forms, all the phosphate has been removed. Add about 0.5 gram of solid $\text{NH}_4\text{Cl}$ , heat to boiling, add a slight excess of dilute $\text{NH}_3$ solution ( <i>i.e.</i> until the odour of ammonia is permanent in the boiling solution), boil for 2–3 minutes and filter.		
	<table> <tr> <td data-bbox="272 645 681 797"><b>Residue.</b> Examine for Group IIIA. The excess of Zr will be found in the residue after treatment with <math>\text{H}_2\text{O}_2</math> and <math>\text{NaOH}</math> solution (or with sodium perborate <math>\text{NaBO}_3 \cdot 4\text{H}_2\text{O}</math> and boiling), and will accompany any Fe, if present.</td><td data-bbox="686 645 865 797"><b>Filtrate.</b> Examine for Groups IIIB, IV and V.</td></tr> </table>	<b>Residue.</b> Examine for Group IIIA. The excess of Zr will be found in the residue after treatment with $\text{H}_2\text{O}_2$ and $\text{NaOH}$ solution (or with sodium perborate $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ and boiling), and will accompany any Fe, if present.	<b>Filtrate.</b> Examine for Groups IIIB, IV and V.
<b>Residue.</b> Examine for Group IIIA. The excess of Zr will be found in the residue after treatment with $\text{H}_2\text{O}_2$ and $\text{NaOH}$ solution (or with sodium perborate $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ and boiling), and will accompany any Fe, if present.	<b>Filtrate.</b> Examine for Groups IIIB, IV and V.		

**Notes.** (1) It is essential that the acidity with respect to hydrochloric acid should not exceed *N*, otherwise a turbid supernatant liquid is obtained and the removal of phosphate is not quite complete. Test with methyl violet or any other suitable indicator (brilliant cresyl blue, cresol red, etc.).

(2) It is important that the excess of the zirconium nitrate reagent should not exceed 25 per cent, otherwise a turbid supernatant liquid will be obtained; this turbidity cannot be removed by filtration or centrifugation. It is best, therefore, to add the zirconium nitrate solution slowly and with stirring until precipitation appears complete, heat just to boiling, filter, and test the filtrate with the reagent, etc.

(3) The addition of half a Whatman filtration accelerator (or a little filter paper pulp) assists filtration; the precipitate must be washed thoroughly with hot water.

## V, 10. ANALYSIS OF A LIQUID (SOLUTION)

If a liquid is supplied for analysis, proceed as follows:

(1) Observe the colour, odour and any special physical properties.

(2) Test its reaction towards litmus paper.

- (a) *The solution is neutral*: free acids, free bases, acid salts, and salts which give an acid or alkaline reaction owing to hydrolysis, are absent.
- (b) *The solution reacts alkaline*: this may be due to the hydroxides of the alkali and alkaline earth metals, to the carbonates, sulphides, hypochlorites and peroxides of the alkali metals, etc.
- (c) *The solution reacts acid*: this may be due to free acids, acid salts, salts which yield an acid reaction because of hydrolysis, or to a solution of salts in acids.

(3) Evaporate a portion of the liquid to dryness on the water bath (use a porcelain dish and stand it on a beaker half filled with water, the latter being heated by a Bunsen burner); carefully smell vapours evolved from time to time. If a solid residue remains, examine as detailed above for a solid substance. If a liquid remains, evaporate cautiously on a wire gauze in the fume cupboard; a solid residue should then be examined in the usual way. If no residue remains, then the liquid consists of some volatile substance which may be water or water containing certain gases or volatile substances, such as  $\text{CO}_2$ ,  $\text{NH}_3$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{H}_2\text{O}_2$  or  $(\text{NH}_4)_2\text{CO}_3$ , all of which can be readily detected by special tests. It is best to neutralise with sodium carbonate and test for acid radicals (anions).

## CHAPTER VI

### INTRODUCTION TO SYSTEMATIC SEMIMICRO QUALITATIVE INORGANIC ANALYSIS

**VI, 1. Preliminary Discussion.**—It is assumed that the student is already familiar with the operations (ignition tests, blowpipe tests, flame tests, borax bead tests, precipitation, filtration, evaporation, etc.) described in Sections II, 1 and II, 2. A detailed description of semimicro apparatus and of semimicro analytical operations is given in Section II, 3. The student should read this carefully and thus acquire a general knowledge of semimicro technique. To secure the introductory practical experience the following course of instruction may be followed. Reactions are normally carried out in 4 ml. test-tubes or in 3 ml. centrifuge tubes, unless otherwise stated. The solutions employed in testing for cations or anions contain 10 mg. of cation or anion per ml. For purposes of calculation a drop of solution may be assumed to have a volume of 0.05 ml.: this will help in rough computations as to volumes required in adding excess of reagents, etc.

For the cations, a limited number of preliminary reactions should be studied first, followed by an analysis of a mixture or solution containing a member or members of each group. This will give practical experience in the routine operations of semimicro analysis and also provide practice from the very outset in the use of Group Separation Tables. Particular attention should be paid to:

- (i) the exact experimental conditions of the reaction;
- (ii) the colour and physical characteristics (*e.g.* whether crystalline, amorphous or gelatinous) of each precipitate; and
- (iii) the solubility of each precipitate in excess of precipitant, or in solutions of other reagents.

The student should, as far as possible, represent the chemical reactions by ionic equations and then check the equations against the molecular equations given in Chapters III and IV. In this way excellent practice will be obtained in writing and balancing equations, and also help to impress the reactions upon the memory.

To illustrate the manner in which the simple reactions should be carried out, a few selected examples will be given.

#### LEAD ION, $Pb^{++}$

**1. Dilute Hydrochloric Acid.** Place 2 drops of the test solution in a 3 ml. centrifuge tube, and add 2-3 drops of dilute HCl. Note the colour and characteristics of the precipitate. Centrifuge the mixture, balancing the tube with another similar tube containing an approximately equal volume of water. Remove the supernatant liquid, termed the *centrifugate*, by means of a capillary dropper to another tube, and test with a further drop of dilute HCl to ensure that precipitation is complete: if this is so, discard the solution. Treat the precipitate, usually termed the *residue*, with 2 drops of water, stir and centrifuge. Reject the solution, called the *washings*. Add 5-6 drops of water to the washed residue, stir and place the tube containing it in the rack in the boiling water bath. Stir frequently whilst heating. Observe that the precipitate dissolves completely. Cool the clear solution in a stream of water from the cold water tap: observe that colourless crystals of  $PbCl_2$  separate.

**3. Dilute Sulphuric Acid.** To 2 drops of the test solution in a 3 ml. centrifuge tube or 4 ml. test-tube, add 2-3 drops of dilute  $H_2SO_4$ . Centrifuge: remove the centrifugate and test for complete precipitation with 1 drop of dilute  $H_2SO_4$ . Wash the precipitate with 2-3 drops of water, centrifuge and discard the washings. Now introduce 2-3 drops of ammonium acetate solution and stir: the precipitate will dissolve.

**4. Potassium Chromate Solution.** Treat 2 drops of the test solution with 1-2 drops of  $K_2CrO_4$  solution. Note the formation of a yellow precipitate. Centrifuge and wash. Add 2 drops of dilute acetic acid to the precipitate and stir: note that the precipitate does not dissolve.

The above examples should suffice to give a general conception as to how the various reactions should be performed. In the reactions involving the passage of hydrogen sulphide into a solution, the apparatus depicted in Fig. II, 3, 17 should be used.

**VI, 2. Abbreviated Course of Instruction.**—The following preliminary reactions, etc., should be carried out by the student. In the case of anions, those marked with an asterisk may be omitted when an elementary course is required: the final decision should be made by the teacher.

## REACTIONS OF THE CATIONS

**Pb<sup>++</sup>.** Section III, 2, reactions 1, 2, 3, 4; blowpipe test.

**Hg<sub>2</sub><sup>++</sup>.** Section III, 3, reactions 1, 6, 7.

**Ag<sup>+</sup>.** Section III, 4, reactions 1, 2, 3; blowpipe test.

Identification of a metal in the solution supplied by the teacher by means of Table SMI (Section III, 5).

**Hg<sup>++</sup>.** Section III, 6, reactions 1, 2, 3; dry test.

**Bi<sup>+++</sup>.** Section III, 7, reactions 1, 3, 5, 6, 10.

**Cu<sup>++</sup>.** Section III, 8, reactions 1, 2, 3, 4, 5, 8; dry test.

**Cd<sup>++</sup>.** Section III, 9, reactions 1, 3, 4; dry test.

Identification of a metal or metals in the solution supplied by means of Table SMIIA (Section III, 10).

**As (ous).** Section III, 11, reactions 1, 2, 3.

**As (ic).** Section III, 12, reactions 1, 2, 3, 4.

**Sb (ous).** Section III, 14, reactions 1, 2, 8.

**Sn<sup>++</sup>.** Section III, 16, reactions 1, 2, 3.

**Sn<sup>++++</sup>.** Section III, 17, reactions 1, 3, 4.

Identification of a metal or metals in the solution supplied by means of Table SMIIIA (Section III, 18).

**Fe<sup>++</sup>.** Section III, 19, reactions 1, 2, 3, 4, 6, 7, 8.

**Fe<sup>+++</sup>.** Section III, 20, reactions 1, 2, 3, 4, 5, 6, 10.

**Al<sup>+++</sup>.** Section III, 21, reactions 1, 2, 3, 7; dry test.

**Cr<sup>+++</sup>.** Section III, 22, reactions 1, 2, 3, 6; dry test (iii).

Identification of a metal or metals in the solution supplied by means of Table SMIV (Section III, 23).

**Co<sup>++</sup>.** Section III, 24, reactions 1, 2, 3, 5, 6, 7; dry test (ii).

**Ni<sup>++</sup>.** Section III, 25, reactions 1, 2, 3, 6, 7, 8; dry test (ii).

**Mn<sup>++</sup>.** Section III, 26, reactions 1, 2, 3, 5, 7; dry test (ii).

**Zn<sup>++</sup>.** Section III, 27, reactions 1, 2, 3, 6, 8, 9; dry test.

Identification of a metal or metals in the solution supplied by means of Table SMV (Section III, 28).

**Ba<sup>++</sup>.** Section III, 29, reactions 1, 2, 3, 4, 6; dry test.

**Sr<sup>++</sup>.** Section III, 30, reactions 1, 2, 3, 5, 6; dry test.

**Ca<sup>++</sup>.** Section III, 31, reactions 1, 2, 3, 5, 6; dry test.

Identification of a metal or metals in the solution supplied by means of Table SMVI (Section III, 32).

**Mg<sup>++</sup>.** Section III, 33, reactions 1, 2, 3, 5, 7, 8; dry test.

**K<sup>+</sup>.** Section III, 34, reactions 1, 2; dry test.

**Na<sup>+</sup>.** Section III, 35, reaction 1; dry test.

**NH<sub>4</sub><sup>+</sup>.** Section III, 36, reactions 1, 3, 7; dry test.

Identification of a metal or metals in the solution supplied by means of Table SMVII (Section III, 37).

## REACTIONS OF THE ANIONS

- $\text{CO}_3^{--}$ . Section IV, 2, reactions 1, 2.  
 $\text{HCO}_3^-$ . Section IV, 3, reactions (i), (ii), (iii).  
 $\text{SO}_3^{--}$ . Section IV, 4, reactions 1, 2, 4, 5, 9, 10.  
 $\text{S}_2\text{O}_3^{--}$ . Section IV, 5, reactions 1, 2, 4, 6, 8.  
 $\text{S}^{--}$ . Section IV, 6, reactions 1, 2, 3, 5, 6.  
 $\text{NO}_2^-$ . Section IV, 7, reactions 1, 2, 7, 10.  
 $\text{CN}^-$ . Section IV, 8, reactions 1, 2, 3, 4, 6.  
 $\text{SCN}^-$ . Section IV, 10, reactions 1, 2, 3, 6, 8.  
 $\text{Cl}^-$ . Section IV, 14, reactions 1, 2, 3.  
 $\text{Br}^-$ . Section IV, 15, reactions 1, 2, 5, 8.  
 $\text{I}^-$ . Section IV, 16, reactions 1, 2, 4, 7, 9.  
 $\text{F}^-$ . Section IV, 17, reactions 1, 2, 6.  
 $\text{NO}_3^-$ . Section IV, 18, reactions 1, 2, 3, 4.  
 $\text{ClO}_3^-$ . Section IV, 19, reactions 1, 2, 3, 6, 7, 10.  
 $\text{B}_4\text{O}_7^{--}$  (borate). Section IV, 23, reactions 1, 2, 3, 8.  
 $\text{SO}_4^{--}$ . Section IV, 24, reactions 1, 2, 5, 6.  
 $\text{PO}_4^{--}$ . Section IV, 28, reactions 1, 3, 4, 5, 6.  
 $\text{CrO}_4^{--}$ . Section IV, 33, reactions 1, 2, 3, 5, 6.  
 $\text{C}_2\text{H}_3\text{O}_2^-$  (acetate). Section IV, 35, reactions 1, 2, 3, 4, 6.  
 $\text{C}_2\text{O}_4^{--}$  (oxalate). Section IV, 37, reactions 1, 2, 3, 4, 5.

## VI, 3. Systematic Analysis. General Considerations.—

The student must realise that the object of qualitative analysis is not simply to detect the constituents of a given mixture; an equally important aim is to ascertain the approximate relative amounts of each component. For this purpose about 0.2 gram of material is usually employed for the analysis: the relative magnitudes of the various precipitates will provide a rough guide as to the proportions of the constituents present.

Every analysis is divided into three parts:

(1) *The preliminary examination.* This includes preliminary examination by dry tests, examination of the volatile products with sodium hydroxide solution (for ammonium), and with dilute and concentrated sulphuric acid (for acid radicals or anions). A special preliminary test for nitrate and/or nitrite is also made here.

(2) *The examination for acid radicals (or anions) in solution.*

(3) *The examination for metal ions (or cations) in solution.*

## VI, 4.

## PRELIMINARY TESTS

**Test (i). Heating in a closed tube.**—Place about 5 mg. of the substance in a dry ignition tube ( $70 \times 4\text{--}5$  mm.) so that none of it remains adhering to the sides and heat cautiously with a semimicro burner; the tube should be held in an almost

Observation	Inference
<p>(a) <b>A gas or vapour is evolved.</b></p> <ol style="list-style-type: none"> <li>1. Water is evolved; test with litmus paper.  The water is alkaline. The water is acid.</li> <li>2. Oxygen is evolved (rekindles a glowing splint).</li> <li>3. Nitrous oxide (rekindles a glowing splint) and steam are evolved.</li> <li>4. Dark brown or reddish fumes (oxides of nitrogen); acidic in reaction.</li> <li>5. Carbon dioxide is evolved (lime water is rendered turbid).</li> <li>6. Ammonia is evolved (turns red litmus paper blue).</li> <li>7. Sulphur dioxide is evolved (odour of burning sulphur; turns potassium dichromate paper green; decolourises fuchsin solution.)</li> <li>8. Hydrogen sulphide is evolved (odour of rotten eggs; turns lead acetate paper black or cadmium acetate paper yellow).</li> <li>9. Chlorine is evolved (yellowish-green gas; bleaches litmus paper; turns potassium iodide-starch paper blue); <i>very poisonous</i>.</li> <li>10. Bromine is evolved (reddish-brown vapour; choking odour; turns fluorescein paper red).</li> <li>11. Iodine is evolved (violet vapours condensing to black crystals).</li> </ol>	<p>Compounds with water of crystallisation (often accompanied by change of colour), ammonium salts, acid salts and hydroxides. Ammonium salts. Readily decomposable salts of strong acids. Nitrates, chlorates and certain oxides. Ammonium nitrate or nitrate mixed with an ammonium salt. Nitrates or nitrites of heavy metals. Carbonates or bicarbonates. Ammonium salts. Normal and acid sulphites; thiosulphates; certain sulphates. Hydrated sulphides or sulphides in the presence of water. Unstable chlorides, <i>e.g.</i> of copper; chlorides in the presence of oxidising agents. Sources similar to chlorine. Free iodine and certain iodides.</p>
<p>(b) <b>A sublimate is formed.</b></p> <ol style="list-style-type: none"> <li>1. White sublimate.*</li> <li>2. Grey sublimate, easily rubbed to globules.</li> <li>3. Steel-grey sublimate; garlic odour.</li> <li>4. Yellow sublimate.</li> </ol>	<p>Ammonium and mercuric salts; <math>As_2O_3</math>; <math>Sb_2O_3</math>. <math>Hg</math>. <math>As</math>. <math>S</math> (melts on heating), <math>As_2S_3</math>, <math>HgI_2</math> (red when rubbed with a glass rod).</p>

\* If a white sublimate forms, heat with four times the bulk of anhydrous  $Na_2CO_3$  and a little  $KCN$  in an ignition tube. A grey mirror, convertible into globules on rubbing with a glass rod, indicates  $Hg$  (*Note: Hg vapour is very poisonous*); a brownish-black mirror, yielding a white sublimate and an odour of garlic when heated in a wide tube, indicates  $As$ ; ammonia evolved (test with mercurous nitrate paper) indicates *ammonium salts*.

horizontal position. Raise the temperature gradually and carefully note any changes which take place.

### Test (ii). Charcoal block reductions.

(a) Heat a little of the substance (say, 2–3 mg.) in a small cavity in a charcoal block in a blowpipe flame.

Observation	Inference
1. The substance decrepitates. 2. The substance deflagrates.	Crystalline salts, <i>e.g.</i> NaCl, KCl. Oxidising agents, <i>e.g.</i> nitrates, nitrites and chlorates. Apply test (b) below.
3. The substance is infusible or incandescent, or forms an incrustation upon the charcoal.	

(b) Mix the substance (3–5 mg.) with twice its bulk of anhydrous sodium carbonate, place it in a cavity in a charcoal block, and heat in the reducing flame of the blowpipe.

Observation	Inference
1. Incrustation without metal: White, yellow when hot. White, garlic odour. Brown.	ZnO. As <sub>2</sub> O <sub>3</sub> . CdO.
2. Incrustation with metal: White incrustation; brittle metal. Yellow incrustation; brittle metal. Yellow incrustation; grey and soft metal, marks paper.	Sb. Bi. Pb.
3. Metal without incrustation: Grey metallic particles, attracted by magnet. Malleable beads.	Fe, Ni, Co. Ag and Sn (white); Cu (red flakes).

**Test (iii). Flame colorations.**—Place 2–3 milligrams of the substance in a depression of a spot-plate, moisten with a few drops of concentrated hydrochloric acid, and introduce a little of the substance on a *clean* platinum wire into the base of a non-luminous flame of a semimicro burner. Alternatively, dip the platinum wire into concentrated hydrochloric acid contained in a depression of a spot plate and then into the substance; sufficient will adhere to the platinum wire for the test to be carried out.



Observation	Inference
Persistent golden-yellow flame.	Na.
Violet (lilac) flame (crimson through cobalt-blue glass).	K.
Brick-red (yellowish-red) flame.	Ca.
Crimson flame.	Sr.
Yellowish-green flame.	Ba.
Livid-blue flame (wire slowly corroded).	Pb, As, Sb, Bi, Cu.

The sodium flame masks that of other elements, *e.g.* that of potassium. Mixtures can be readily detected with a direct-vision spectroscope (see Section II, 1, 4). A less delicate method is to view the flame through two thicknesses of cobalt-blue glass, whereby the yellow colour due to sodium is masked or absorbed; potassium then appears crimson.

**Test (iv). Borax bead reactions.**—Make a borax bead in a loop of platinum wire by dipping the hot wire into borax and heating until colourless and transparent. Bring a *minute* quantity of the substance into contact with the hot bead and heat in the outer or oxidising flame. Observe the colour when the bead is hot and also when it is cold. Heat the bead in the inner or reducing flame and observe the colour in the hot and cold states. Coloured beads are obtained with compounds of copper, iron, chromium, manganese, nickel and cobalt; the most characteristic result is for cobalt.

Oxidising flame	Reducing flame	Metal
1. Green when hot; blue when cold.	Colourless when hot, opaque-red when cold.	Cu.
2. Yellow, hot and cold.	Green, hot and cold.	Fe.
3. Dark yellow when hot, green when cold.	Green, hot and cold.	Cr.
4. Violet (amethyst), hot and cold.	Colourless, hot and cold.	Mn.
5. Blue, hot and cold.	Blue, hot and cold.	Co.
6. Reddish-brown when cold.	Grey when cold.	Ni.

**Test (v). Test for ammonium radical.**—Mix 4–5 mg. of the substance with about 0.2 ml. (say, 4–5 drops) of sodium hydroxide solution in a semimicro test-tube, introduce a Pyrex filter tube carrying a strip of red litmus paper and place the assembly (Fig. II, 3, 19, *a*) in the hot water rack (Fig. II, 3, 13). The evolution of ammonia, detected by its action upon the reagent paper, indicates the presence of an *ammonium salt*.

Filter paper moistened with mercurous nitrate solution may also be used: this is blackened by ammonia. The mercurous nitrate reagent contains an excess of free nitric acid; it is advisable, therefore, to add sodium carbonate solution dropwise and with stirring to about 1 ml. of mercurous nitrate solution until a *slight* permanent precipitate is produced: the solution is centrifuged and the centrifugate is employed for the preparation of mercurous nitrate paper.

Alternatively, drop-reaction paper treated with 2-3 drops of 5 per cent tannic acid solution and 2-3 drops of 20 per cent silver nitrate solution may be used: it is blackened by ammonia.

*Note.* Sodium hydroxide is a dangerous substance because of its destructive action upon the eyes. Great care should be taken that the test-tube containing the hot sodium hydroxide solution, particularly in test (vi), is directed away from the eyes of the observer and his near neighbours. The solution, when heated directly, has a tendency to "bump."

**Test (vi). Test for nitrate (or nitrite).**—If ammonium is found, transfer the solution from test (v) with the aid of 0.5 ml. of water to a semimicro boiling tube (or crucible), add 0.5 ml. of sodium hydroxide solution and evaporate down to a volume of about 0.2 ml.—this treatment completely decomposes the ammonium salt. Transfer the residue to a semimicro test-tube, rinse the vessel with 0.5 ml. of sodium hydroxide solution and add this to the contents of the test-tube. Then add 10 mg. of Devarda's alloy (or of aluminium powder or thin foil), introduce a Pyrex filter tube provided with a loose plug of cotton wool at the lower end and containing a strip of red litmus paper or mercurous nitrate paper (Fig. II, 3, 19, a), and place the assembly in the hot water rack. If frothing occurs, remove the apparatus from the water bath until the vigorous reaction has subsided.

If ammonium is absent, add about 10 mg. of Devarda's alloy (or of aluminium as powder or thin foil) and 0.2-0.3 ml. of sodium hydroxide solution to the reaction mixture from test (v), introduce the filter tube carrying the reagent paper and proceed as above.

If ammonia is evolved, as detected by its action upon red litmus paper or upon mercurous nitrate paper, the presence of a *nitrate or nitrite* is indicated. Nitrite will also be detected in the reaction with dilute sulphuric acid {see test (vii)}: if nitrite is absent, the presence of nitrate is established.

It must be emphasised that both the mercurous nitrate paper test and the tannic acid-silver nitrate paper test is not applicable in the presence of arsenites. Arsenites are reduced under the above conditions to arsine, which also blackens the test papers.

**Test (vii). Action of dilute sulphuric acid.**—Treat 5–10 mg. of the substance in a semimicro test-tube with about 0.3–0.5 ml. of 2*N* sulphuric acid and note whether any reaction takes place in the cold (indicated by *C*). Heat the mixture on a water bath and observe the effect produced.

Observation	Inference
1. Colourless gas is evolved with effervescence; gas is odourless and produces a turbidity when passed into lime water (see Fig. II, 3, 19). ( <i>C</i> )	CO <sub>2</sub> from <i>carbonate</i> or <i>bicarbonate</i> .
2. Nitrous fumes evolved; recognised by red-dish-brown colour and odour. ( <i>C</i> )	NO <sub>2</sub> from <i>nitrite</i> .
3. Yellowish-green gas evolved; suffocating odour, reddens then bleaches litmus paper, also turns starch-KI paper blue; <i>very poisonous</i> . ( <i>C</i> )	Cl <sub>2</sub> from <i>hypochlorite</i> .
4. Colourless gas evolved with suffocating odour; turns filter paper moistened with K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> solution green; decolourises fuchsin solution.	SO <sub>2</sub> from <i>sulphite</i> .
5. Colourless gas evolved; gives above tests for SO <sub>2</sub> ; sulphur is deposited in the solution.	SO <sub>2</sub> and S from <i>thio-sulphate</i> .
6. Colourless gas evolved; odour of rotten eggs; blackens filter paper moistened with lead acetate solution; turns cadmium acetate paper yellow.	H <sub>2</sub> S from <i>sulphide</i> .*
7. Odour of vinegar.	H.C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> from <i>acetate</i> .
8. Colourless gas is evolved; rekindles glowing splint.	O <sub>2</sub> from <i>peroxides</i> or <i>per-salts</i> of alkali and alkaline earth metals.
9. Colourless gas evolved; odour of bitter almonds,† <i>highly poisonous</i> .	HCN from <i>cyanide</i> or from soluble <i>ferri-</i> and <i>ferro-cyanides</i> .
10. Upon boiling, yellow solution formed and SO <sub>2</sub> (fuchsin solution decolourised, etc.) evolved.	SO <sub>2</sub> , etc., from <i>thio-cyanate</i> .

**Test (viii). Action of concentrated sulphuric acid.**—Treat 5–10 mg. of the substance in a semimicro test-tube with 0.3–0.5 ml. of concentrated sulphuric acid. If no reaction occurs in the cold, place the tube in the hot water rack. (If

\* Many sulphides, especially native ones, are not affected by dilute H<sub>2</sub>SO<sub>4</sub>; some H<sub>2</sub>S is evolved by warming with concentrated HCl alone or with a little tin.

† If cyanide is suspected, gently warm (water bath) 5 mg. of the mixture with 5 drops of 2*N* H<sub>2</sub>SO<sub>4</sub> in a semimicro test-tube carrying over the mouth a piece of filter paper moistened at the centre with 1 drop of dilute NaOH solution. After 2 minutes, treat the drop on the paper with 1 drop of FeSO<sub>4</sub> solution, warm and add a drop or two of 6*N* HCl. A blue colour indicates the presence of a cyanide. For another test, see Section IV, 8, reaction 1. Mercuric cyanide is attacked slowly.

chlorate is suspected from the preliminary charcoal reduction test to be present, use not more than 5 mg. for this test, as an explosion may result on warming.)

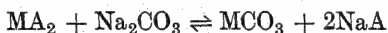
If the substance reacted with dilute sulphuric acid, the addition of the concentrated acid may result in a vigorous reaction and rapid evolution of gas, which may be accompanied by a very fine spray of acid. In such a case it is best to add dilute (2*N*) sulphuric acid from a capillary dropper to another portion of the substance until action ceases, and then to add 1 ml. of concentrated sulphuric acid.

Observation	Inference
1. Colourless gas evolved with pungent odour and which fumes in the air; white fumes of $\text{NH}_4\text{Cl}$ in contact with glass rod moistened with concentrated $\text{NH}_3$ solution; $\text{Cl}_2$ evolved on addition of $\text{MnO}_2$ (reddens then bleaches litmus paper).	$\text{HCl}$ from <i>chloride</i> .
2. Gas evolved with pungent odour, reddish colour and fumes in moist air; on addition of $\text{MnO}_2$ , increased amount of red fumes with odour of $\text{Br}_2$ (fumes colour filter paper moistened with fluorescein solution red).	$\text{HBr}$ and $\text{Br}_2$ from <i>bromide</i> .
3. Violet vapours evolved, accompanied by pungent acid fumes, and often $\text{SO}_2$ and even $\text{H}_2\text{S}$ .	$\text{HI}$ and $\text{I}_2$ from <i>iodide</i> .
4. Yellow gas evolved in the cold with characteristic odour; explosion or crackling noise on warming <i>gently</i> (DANGER!).	$\text{ClO}_2$ from <i>chlorate</i> .
5. "Oily" appearance of tube in cold; on warming, pungent gas evolved, which corrodes the glass; if moistened glass rod introduced into the vapour, a gelatinous precipitate of hydrated silica is deposited upon it.	$\text{HF}$ from <i>fluoride</i> .
6. Pungent acid fumes evolved, often coloured brown by $\text{NO}_2$ ; colour deepens upon addition of copper turnings (if nitrite absent).	$\text{HNO}_3$ and $\text{NO}_2$ from <i>nitrate</i> .
7. Yellow coloration in cold; upon warming, vigorous reaction, $\text{COS}$ (burns with blue flame), $\text{SO}_2$ (decolourises fuchsin solution) and free $\text{S}$ produced.	$\text{COS}$ , $\text{SO}_2$ and $\text{S}$ from <i>thiocyanate</i> .
8. Colourless gas evolved; burns with a blue flame;* no charring ( <i>very poisonous</i> ).	$\text{CO}$ from <i>formate</i> .
9. Colourless gas evolved; renders lime water turbid and may also burn with a blue flame; no blackening.	$\text{CO}$ and $\text{CO}_2$ from <i>oxalate</i> .

\* The burning splint should be introduced *into* the tube; the application of a flame to the mouth of the tube frequently fails to ignite the gas owing to its dilution with air in the tube.

## VI, 5. EXAMINATION FOR ACID RADICALS (ANIONS) IN SOLUTION

The preliminary tests (vii) and (viii) with dilute sulphuric acid and with concentrated sulphuric acid will have provided useful information as to many acid radicals present. For more detailed information, it is necessary to have a solution containing all (or most) anions free from heavy metal ions. This is best prepared by boiling the substance with concentrated sodium carbonate solution; double decomposition occurs (either partially or completely) with the production of the insoluble carbonates\* of the metals (other than alkali metals) and the soluble sodium salts of the anions, which pass into solution. Thus, if the unknown substance is the salt of a bivalent metal M and an acid HA, the following reaction will occur:



The carbonate  $\text{MCO}_3$  is insoluble and the sodium salt NaA will pass into solution whether  $\text{MA}_2$  is soluble in water or not.

**Preparation of solution for testing for anions.**—Boil 200 mg. of the finely divided substance or mixture with 2.5 ml. of a saturated solution of pure sodium carbonate† (prepared from 0.4 gram of anhydrous sodium carbonate and 2.5 ml. of distilled water) for 5–10 minutes in a 10 ml. conical flask with a funnel in the mouth to reduce the loss by evaporation.‡ Transfer, with the aid of about 0.5 ml. of water, to a 4 ml. semimicro test-tube and centrifuge. Remove the centrifugate to another test-tube: add 1 ml. of hot distilled water to the residue, stir and add the clear washings to the original centrifugate; the total volume should be 3–4 ml. The sodium carbonate extract will be termed the “ $\text{Na}_2\text{CO}_3$  prepared solution.” Use the solution to carry out the following tests.

**1. Sulphate test.**—To 5 drops of the “ $\text{Na}_2\text{CO}_3$  prepared solution” in a 4 ml. test-tube add dilute hydrochloric acid until acid (test with litmus paper) and then add 3 drops in excess. Place in the hot water rack for 5 minutes to expel carbon di-

\* Certain carbonates, initially formed, are converted into insoluble basic carbonates or into hydroxides.

† It is essential to use pure sodium carbonate; the A.R. solid is satisfactory. Some “pure” samples may contain traces of sulphate or chloride: the absence of these impurities should be confirmed by a blank experiment.

‡ If no precipitate is obtained, the substance is virtually free from heavy metals, and the sodium carbonate treatment may be omitted if more of the solution is required.

oxide completely, and then add 2–3 drops of barium chloride solution. A white precipitate ( $\text{BaSO}_4$ ) shows the presence of *sulphate*.

**2. Test for reducing agents.**—Acidify 5 drops of the “ $\text{Na}_2\text{CO}_3$  prepared solution” with dilute sulphuric acid and add 3 drops of dilute sulphuric acid in excess. Add 2–3 drops of 0.02N potassium permanganate solution (prepared by dilution of 1 drop of 0.1N  $\text{KMnO}_4$  with 4 drops of water and mixing well). Bleaching of the permanganate solution indicates the presence of one or more of the following reducing anions: *sulphite*, *thiosulphate*, *sulphide*, *nitrite*, *bromide*, *iodide* and *arsenite*. If the permanganate is not decolourised, place the tube in the hot water rack for several minutes and observe the result. If the reagent is bleached only on heating, the presence of *oxalate* is indicated. A negative test shows the absence of the above anions.

**3. Test for oxidising agents.**—Acidify 5 drops of the “ $\text{Na}_2\text{CO}_3$  prepared solution” cautiously with concentrated hydrochloric acid and add 2 drops in excess, followed by 3–5 drops of the manganous chloride reagent. Place in the hot water rack for 1 minute. A brown (or black) coloration indicates the presence of *nitrate*, *nitrite*, *chlorate* or *chromate*. A negative test indicates the absence of the above oxidising anions except for small amounts of nitrates or nitrites. If reducing anions have been found, the test is inconclusive.

*Note.* The reagent consists of a saturated solution of manganous chloride,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ , in concentrated hydrochloric acid. Its action depends upon its conversion by even mild oxidising agents to a dark-brown coloured manganic salt, probably containing the complex  $[\text{MnCl}_6]^{3-}$  or  $[\text{MnCl}_4]^-$  ions.

**4. Tests with silver nitrate solution.**—Sulphide, cyanide and sulphite interfere in tests with silver nitrate solution, hence if any of these anions was detected in the preliminary test with dilute sulphuric acid, it must be removed first as follows. Acidify 1 ml. of the “ $\text{Na}_2\text{CO}_3$  prepared solution” with dilute acetic acid (use litmus paper) and boil *gently* in a small conical flask or crucible in the fume cupboard to expel  $\text{H}_2\text{S}$ ,  $\text{HCN}$  or  $\text{SO}_2$  (1–2 minutes). It is important that the solution be acid throughout. Centrifuge, if necessary, and allow to cool. If the volume has been reduced appreciably, add water to restore the original volume (solution S).

Acidify 1.0 ml. of the " $\text{Na}_2\text{CO}_3$  prepared solution" cautiously with dilute  $\text{HNO}_3$  (use litmus paper). Determine the total volume of the acidified solution (or of solution *S*) with the aid of a small measuring cylinder or calibrated 2 ml. pipette, add one-tenth of the volume of concentrated  $\text{HNO}_3$  and stir for 10–15 seconds. Then add a few drops of  $\text{AgNO}_3$  solution with stirring. If a precipitate forms, place the test-tube or centrifuge tube in the hot water rack and add  $\text{AgNO}_3$  solution slowly and with stirring until precipitation is complete. Centrifuge and wash with a few drops of *N*  $\text{HNO}_3$ .

**Residue.**  
 $\text{AgCl}$ —white.  
 $\text{AgBr}$ —pale  
 yellow.  
 $\text{AgI}$ —yellow.  
 $[\text{AgSCN}$ —  
 white.]

**Centrifugate.** Add 3–4 drops of  $\text{AgNO}_3$  solution, then 1–2 drops of 20%  $\text{NaNO}_3$  solution (prepared from the A.R. solid) and stir. If a white ppt. ( $\text{AgCl}$ ) forms, *chlorate* is present: continue the addition of  $\text{NaNO}_3$  solution drop-wise until precipitation is complete. [If no ppt. forms, do not add more  $\text{NaNO}_3$  solution.] Centrifuge, if necessary, and wash with 2 drops of *N*  $\text{HNO}_3$ .

**Residue.**  
 $\text{AgCl}$   
 derived  
 from  
 $\text{AgClO}_3$ .

**Centrifugate.** Add  $\text{NaOH}$  solution drop-wise and with vigorous stirring until the solution is just neutral to litmus or, better, barely alkaline to nitrazine yellow indicator (1); then add 2–3 drops of dilute acetic acid and 5 drops of  $\text{AgNO}_3$  solution. Heat to about  $80^\circ\text{C}$  in the water bath (2). If a permanent ppt. forms, add more  $\text{AgNO}_3$  solution until precipitation is complete. Centrifuge, and wash with a few drops of hot water.

**Residue (3).**  
 $\text{Ag}_3\text{PO}_4$ —yellow.  
 $\text{Ag}_3\text{AsO}_4$ —brownish-red.  
 $\text{Ag}_3\text{AsO}_3$ —yellow.  
 $\text{Ag}_2\text{C}_2\text{O}_4$ —white.

**Centrifugate.**  
 Reject.

**Notes.** (1) It is essential that the solution be just neutral to litmus or, at most, barely alkaline; the latter will be indicated by a very slight brown opalescence (due to  $\text{Ag}_2\text{O}$ ) obtained after shaking. If much brown silver oxide separates, it will re-dissolve only with difficulty.

The introduction of 1 drop of nitrazine yellow indicator into the solution is to be preferred. (This indicator covers the *pH* range 5.5–7.2 and the colour change is from yellow to blue.) The addition of  $\text{NaOH}$  solution is continued until the solution just assumes a pale blue colour.

(2) Silver acetate is soluble in hot water and is thus held in solution.

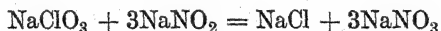
(3) If chromate is present (yellow or orange solution), it will be reduced by the  $\text{NaNO}_2$  treatment and will be precipitated here as green chromic hydroxide. *Chromate* is readily detected in the

" $\text{Na}_2\text{CO}_3$  prepared solution" as follows. Acidify 5 drops of the solution with dilute  $\text{HNO}_3$  and cool. Add 0.3 ml. of amyl alcohol and 2 drops of 3 per cent  $\text{H}_2\text{O}_2$  solution. A blue coloration ("perchromic acid") in the organic layer confirms chromate.

The separations described in the above table are based upon the following facts:

(i)  $\text{AgNO}_3$  solution precipitates only  $\text{AgCl}$ ,  $\text{AgBr}$  and  $\text{AgI}$  from a dilute nitric acid solution, the other silver salts being soluble.

(ii)  $\text{NaNO}_2$  solution reduces chlorate to chloride, which is precipitated as  $\text{AgCl}$  in the presence of  $\text{AgNO}_3$  solution:



(iii) In solutions faintly acid with acetic acid, phosphate, arsenate, arsenite and oxalate are precipitated by  $\text{AgNO}_3$  solution.

If a mixture of halides, or of phosphate, arsenate and arsenite, is suspected, use the methods of separation given in Section VII, 16. The confirmatory tests for the individual anions are collected in Section VI, 6.

The reactions with silver nitrate solution are intended to act as a guide to the presence of groups of anions, and the table must be interpreted in conjunction with the observations made in the preliminary tests. Arsenite, arsenate and chromate will be found in the analysis for cations (Section VI, 8).

**5. Tests with calcium chloride solution.\***—For tests 5 and 6 a " $\text{Na}_2\text{CO}_3$  practically neutral solution" is required. This is obtained as follows. Take 0.5 ml. of the " $\text{Na}_2\text{CO}_3$  prepared solution" in a semimicro boiling tube (or small crucible) and render it faintly acid with dilute nitric acid (use litmus paper). Heat to boiling for about 30 seconds to expel carbon dioxide, etc., allow to cool, then add dilute ammonia solution until just alkaline,† and boil for 30 seconds to expel the slight excess of ammonia. Transfer the " $\text{Na}_2\text{CO}_3$  practically neutral solution" to a semimicro test-tube and divide into two equal parts; reserve half for test 6.

\* Tests 5 and 6 may be omitted by those requiring only a beginner's course in qualitative analysis.

† If a ppt. forms on neutralising the solution, the presence of arsenic, antimony and tin sulphides and possibly salts of amphoteric bases (lead, tin, aluminium and zinc) is indicated. The ppt. should be filtered off and rejected.



Add an equal volume of  $\text{CaCl}_2$  solution and place in the hot water rack for 5 minutes. Centrifuge and wash with a few drops of hot water.

**Residue.** May be calcium fluoride, oxalate, phosphate and arsenate.

Add 1 ml. of dilute acetic acid, heat in the hot water rack for 2-3 minutes and centrifuge.

**Centrifugate.**  
Reject.

**Residue.** May be calcium oxalate and calcium fluoride.

Extract with 1 ml. of hot dilute  $\text{H}_2\text{SO}_4$  and centrifuge, if necessary. Treat the hot centrifugate or solution with 2 drops of 0.02N  $\text{KMnO}_4$  solution. If the permanganate is decolourised, **oxalate is present**. If the ppt. is not completely soluble in dilute  $\text{H}_2\text{SO}_4$ , test the original substance for fluoride by the water-film test (Section VI, 6).

**Centrifugate.** Add  $\text{NaOH}$  solution dropwise until neutral (use litmus or nitrazine yellow indicator).

White ppt. (sometimes separating slowly).

**Arsenate and/or phosphate present.**

Treat the suspension or neutral solution with a few drops of  $\text{AgNO}_3$  solution. A yellow ppt. indicates phosphate: a brownish-red ppt. indicates arsenate or arsenate + phosphate.

**6. Test with ferric chloride solution.**—Treat the other portion of the " $\text{Na}_2\text{CO}_3$  practically neutral solution" from test 5 with a few drops of aqueous  $\text{FeCl}_3$  solution.\*

Reddish-purple coloration indicates *thiosulphate*.

Reddish-brown coloration, yielding a brown precipitate on dilution and boiling in a semimicro boiling tube, indicates *acetate*.

Yellowish-white precipitate indicates *phosphate*.

Blood-red coloration, discharged by  $\text{HgCl}_2$  solution, indicates *thiocyanate*.

## VI, 6. CONFIRMATORY TESTS FOR ACID RADICALS OR ANIONS

The tests in the preceding section will indicate the acid radicals or anions present. In general, these should be confirmed by at least one distinctive confirmatory test. The following are recommended. Full experimental details will be

\* The bench reagent usually contains excess of free acid added during its preparation in order to produce a clear solution; this may prevent the precipitation of the basic acetate on boiling. It is therefore recommended that dilute  $\text{NH}_3$  solution be added dropwise to 1 ml. of side-shelf  $\text{FeCl}_3$  solution until a slight precipitate forms and the mixture centrifuged. The clear centrifugate (sometimes termed "*neutral  $\text{FeCl}_3$  solution*") is employed in the test.

found in Chapter IV under the reactions of the acid radicals (anions); the reference to these will be abbreviated as follows: thus (IV, 2, 7) is to be interpreted as Section IV, 2, reaction 7. It will of course be realised that the tests in Chapter IV refer to reactions on the macro scale; the student should have no difficulty in reducing these to the semimicro scale when once the technique described in Section II, 3 has been acquired. Particular attention is directed to the apparatus shown in Fig. II, 3, 19, which is employed in testing for evolved gases with reagent papers and liquid reagents. It is assumed that interfering anions are absent or have been removed as described in Section VI, 7 under *Special Tests for Mixtures of Acid Radicals (Anions)*.

**Chloride.** Mix 20 mg.\* of the substance with an equal weight of  $\text{MnO}_2$  and 0.5 ml. of concentrated  $\text{H}_2\text{SO}_4$ , and place in the hot water rack;  $\text{Cl}_2$  evolved (reddens then bleaches litmus paper and also turns KI-starch paper blue) (IV, 14, 2).

**Bromide.**  $\text{MnO}_2$  and concentrated  $\text{H}_2\text{SO}_4$  test (as under *Chloride*);  $\text{Br}_2$  evolved (IV, 15, 2) or dissolve 20 mg. of the substance in 0.5 ml. of water, add 5 drops of dilute  $\text{HCl}$ , 5 drops of  $\text{CCl}_4$  and 2–3 drops of  $\text{NaOCl}$  solution and shake; reddish-brown coloration of  $\text{CCl}_4$  layer (IV, 15, 5).

**Iodide.**  $\text{NaOCl}$  solution, dilute  $\text{HCl}$  and  $\text{CCl}_4$  test (as under *Bromide*); violet coloration of  $\text{CCl}_4$  layer (IV, 16, 4).

**Fluoride.** Fit a 4 ml. ( $75 \times 10$  mm.) test-tube with a cork carrying a tube about 8 cm. long and of about 3 mm. bore: cut a V-shaped groove in the cork. Adjust the tube in the cork so that the lower end is about 2.5 cm. from the bottom of the test-tube (compare Fig. VII, 2, 1). Place 15–20 mg. of the substance and 0.5 ml. of concentrated  $\text{H}_2\text{SO}_4$  in the test-tube, dip the glass tube into water so that a film of water almost seals the lower end to a depth of about 5 mm., insert into the test-tube, and place in the hot water rack. The formation of a white film in the water confirms *fluoride* (IV, 17, 1).

The zirconium-alizarin-S test (IV, 17, 6) may be used if oxalate is known to be absent and also in the absence of sulphates, thiosulphates, nitrites, phosphates and arsenates in quantities greater than that of the fluoride.

\* The weights and volumes given in the suggested confirmatory tests are very approximate and serve to indicate a reasonable scale for the various operations. They are given solely for the guidance of the student; *satisfactory results can, however, be obtained on an appreciably smaller scale.*

**Nitrite.** Treat 10–20 mg. of the substance with 0.5 ml. of dilute acetic acid, 10 mg. of thiourea and 3 drops of  $\text{FeCl}_3$  solution. Red coloration (IV, 7, 9).

**Nitrate.** Brown ring test with  $\text{FeSO}_4$  solution and concentrated  $\text{H}_2\text{SO}_4$  (IV, 18, 3) if bromide, iodide, chlorate and nitrite absent. (i) Dissolve 10–20 mg. of the substance in 0.5 ml. of water. Cautiously add 1 ml. of concentrated  $\text{H}_2\text{SO}_4$ , mix and cool under running water. Incline the tube and with great care allow about 0.5 ml. of  $\text{FeSO}_4$  solution to run slowly down the side of the tube so that it forms a layer above the heavy sulphuric acid (Fig. VI, 6, 1). Observe the brown ring

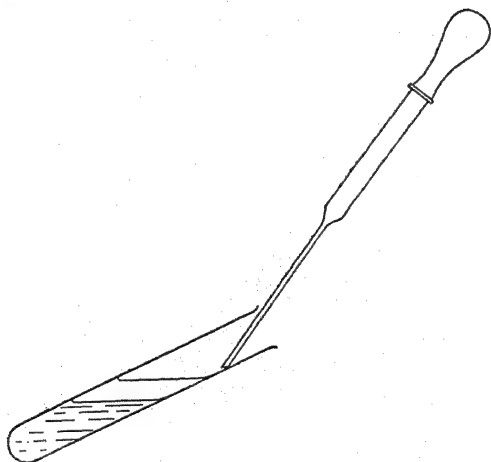


Fig. VI, 6, 1

at the junction of the two liquids after 1–2 minutes. (ii) Dissolve 10–20 mg. of the substance in 0.5 ml. of water and add about 1 ml. of  $\text{FeSO}_4$  solution. Incline the tube and allow 0.5–1 ml. of concentrated  $\text{H}_2\text{SO}_4$  to run slowly down the side of the tube to form a layer under the solution (Fig. VI, 6, 1), and after 1–2 minutes observe the brown ring at the interface.

**Sulphide.** Treat 10–20 mg. of the substance with 0.5 ml. of dilute  $\text{H}_2\text{SO}_4$ . Place the tube in the hot water rack and test with lead or cadmium acetate paper (IV, 6, 1).

**Sulphite.** Treat 10–20 mg. of the substance with 0.5 ml. of dilute  $\text{H}_2\text{SO}_4$ , place the tube in the hot water rack, and test

for  $\text{SO}_2$  with  $\text{K}_2\text{Cr}_2\text{O}_7$  paper\* (Fig. II, 3, 19, a) or with 0.2 ml. of fuchsin solution (Fig. II, 3, 19, b) (IV, 4, 10).

**Thiosulphate.** Dilute  $\text{H}_2\text{SO}_4$  on solid and liberation of  $\text{SO}_2$  ( $\text{K}_2\text{Cr}_2\text{O}_7$  test—details under *Sulphite*) and sulphur (IV, 5, 1).

**Sulphate.** The  $\text{BaCl}_2$  solution and dilute  $\text{HCl}$  test is fairly conclusive.

Further confirmation is obtained as follows. Centrifuge the suspension and remove the supernatant liquid. Add 1 ml. of water, stir, centrifuge and discard the centrifugate. Add 3–4 drops of water, stir thoroughly to produce a fairly uniform suspension, transfer the suspension to a small plug of cotton wool in a small ignition tube, introduce 2–3 drops of  $\text{Na}_2\text{CO}_3$  solution and heat cautiously to redness. Maintain the lower part of the tube at a red heat for 2–3 minutes and allow to cool. Break the tube, transfer the residue as completely as possible to a semimicro test-tube, add 0.5 ml. of dilute  $\text{HCl}$  and introduce a Pyrex filter tube carrying a strip of filter paper moistened with lead acetate solution. Place the assembly in the hot water rack. A brown stain on the paper confirms sulphate.

The lead acetate test on the solution and the dissolution of the resulting precipitate of lead sulphate in ammonium acetate solution are also characteristic (IV, 24, 2).

**Carbonate.** Treat 10–20 mg. of the substance with 0.5 ml. of dilute  $\text{H}_2\text{SO}_4$ , place the tube in the hot water rack, and test with 0.2–0.5 ml. of lime water (Fig. II, 3, 19, b or c) (IV, 2, 1).

**Hypochlorite.** Treat 10–20 mg. of the substance with 0.5 ml. of dilute  $\text{HCl}$ , place the tube in the hot water rack and test for  $\text{Cl}_2$  with  $\text{KI}$ -starch paper and with litmus paper (IV, 13, 4).

**Chlorate.** The  $\text{AgNO}_3$ – $\text{NaNO}_2$  test is conclusive (see table in Section VI, 5, test 5; also IV, 19).

**Chromate.** Mix 10–20 mg. of the substance with 0.5 ml. of dilute  $\text{H}_2\text{SO}_4$ , add 0.5 ml. of amyl alcohol and 0.3 ml. of 10-volume  $\text{H}_2\text{O}_2$ ; blue colour of alcohol layer (IV, 33, 4).

**Arsenite.** Immediate ppt. of  $\text{As}_2\text{S}_3$  in dilute  $\text{HCl}$  solution (III, 11, 1) and absence of ppt. with magnesium nitrate reagent (III, 11, 3).

**Arsenate.** Action of  $\text{H}_2\text{S}$  on acid solution (III, 12, 1),  $\text{AgNO}_3$  solution test in faintly acetic acid solution (III, 12, 2), and magnesium nitrate reagent test (III, 12, 3).

**Phosphate.** Mix 10–20 mg. of the substance with 0.5 ml. of dilute  $\text{HNO}_3$ , add 1 ml. of ammonium molybdate reagent,

\* For the preparation of  $\text{K}_2\text{Cr}_2\text{O}_7$  paper, the dichromate solution should be almost saturated.

and place the tube in the hot-water rack for a minute or two. Yellow ppt. (IV, 28, 4).

**Cyanide.** Prussian blue test (IV, 8, 4) or ammonium sulphide test (IV, 8, 1, 6).

**Thiocyanate.** Ferric chloride solution test; colour discharged by  $\text{HgCl}_2$  solution or by  $\text{NaF}$  solution, but not by  $\text{HCl}$  (IV, 10, 6).

**Borate.** Flame test (IV, 23, 2); or turmeric paper test (IV, 23, 3); or mannitol-bromothymol blue test (IV, 23, 8).

**Acetate.** Mix 20 mg. of the substance with 1 ml. of ethyl or *n*-butyl alcohol and 5 drops of concentrated  $\text{H}_2\text{SO}_4$ . Heat in the hot water rack for 10 minutes, and pour into 2 ml. of  $\text{Na}_2\text{CO}_3$  solution—characteristic odour of ester (IV, 35, 3) OR, better, indigo test (IV, 35, 9). Mix 15 mg. of the substance with 15 mg. of  $\text{CaCO}_3$  in a semimicro test-tube, introduce a pressure-filter tube carrying a strip of filter paper moistened with a solution of 5 mg. of *o*-nitrobenzaldehyde in 1 ml. of  $\text{NaOH}$  solution. Heat the test-tube strongly. Blue or green stain on paper confirms acetate.

**Oxalate.** Precipitate with  $\text{CaCl}_2$  solution in the presence of dilute acetic acid, the precipitate decolourises a dilute acid solution of  $\text{KMnO}_4$  (IV, 37, 3, 4 and VI, 5, 5); resorcinol test (IV, 37, 5).

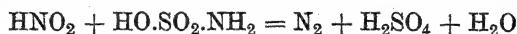
## VI, 7. SPECIAL TESTS FOR MIXTURES OF ACID RADICALS (ANIONS)

The subject is treated fully in Section IV, 45, and again (for elementary students) in Section V, 6, but on a macro scale. The student should be able to adapt these to semimicro work. Some typical semimicro separations of mixtures of anions are given below. The quantities are for guidance only and can be reduced, if desired. If the mixture is insoluble in water, it is often convenient to employ the " $\text{Na}_2\text{CO}_3$  prepared solution" (Section VI, 5) or the " $\text{Na}_2\text{CO}_3$  practically neutral solution" (Section VI, 5, test 5). The special gas testing apparatus of Fig. II, 3, 19 will, of necessity, find application here.

**1. Carbonate in the presence of Sulphite.**—Treat 20 mg. of the mixture with 20 mg. of finely powdered  $\text{K}_2\text{Cr}_2\text{O}_7$  and 0.5 ml. of dilute  $\text{H}_2\text{SO}_4$ ; place the apparatus (Fig. II, 3, 19,

*b* or *c*) in the hot water rack, and test for  $\text{CO}_2$  with lime or baryta water. [The addition of a few mg. of finely divided zinc will generate  $\text{H}_2$  and assist in driving the  $\text{CO}_2$  out of the tube.]

**2. Nitrate in the presence of Nitrite.**—Dissolve 10 mg. of the solid in 1 ml. of water. Remove 1 drop with a glass stirring rod and “spot” on KI-starch paper moistened with very dilute  $\text{H}_2\text{SO}_4$ : a blue colour is obtained, due to the iodine liberated by the nitrous acid. Add 20–30 mg. of sulphamic acid and stir until effervescence ceases:



Test for absence of nitrite by “spotting” on KI-starch paper. Then apply the brown ring test (Section VI, 6).

**3. Nitrate in the presence of Bromide and Iodide.**—Treat 10–15 mg. of the substance with 1 ml. of sodium hydroxide solution and 10–15 mg. of Devarda’s alloy (or of aluminium as powder or as thin foil), place in the hot water rack, and test for ammonia with red litmus paper or mercurous nitrate paper (Fig. II, 3, 19, *a*).

Another procedure is to just acidify 5 drops of the “ $\text{Na}_2\text{CO}_3$  prepared solution” with dilute acetic acid, and then add the ammoniacal silver sulphate reagent (see Section IV, 45, 3) dropwise until precipitation is complete. Centrifuge. Add excess of concentrated  $\text{H}_2\text{SO}_4$  cautiously to the centrifugate and apply the brown ring test.

**4. Nitrate in the presence of Chlorate.**—Test for nitrate as under 3: then acidify with dilute  $\text{HNO}_3$  and test for chloride with a few drops of  $\text{AgNO}_3$  solution.

If chloride is originally present, it may be removed by the addition of saturated silver sulphate solution or of the ammoniacal silver sulphate reagent.

**5. Chloride in the presence of Bromide and Iodide.**—Dissolve 10–20 mg. of the solid in 0.5–1 ml. of water in a semimicro boiling tube (or use 5–10 drops of the “ $\text{Na}_2\text{CO}_3$  prepared solution” acidified with dilute  $\text{HNO}_3$ ), add 1–1.5 ml. of concentrated  $\text{HNO}_3$ , and boil gently until the bromine and iodine are volatilised. Dilute with 1 ml. of water, and test for chloride by the addition of a few drops of  $\text{AgNO}_3$  solution.

Alternatively, repeat the experiment but add 20 mg. of precipitated  $\text{PbO}_2$  instead of the concentrated  $\text{HNO}_3$ . After

the bromine and iodine have been eliminated, add 1 ml. of water, transfer to a centrifuge tube, centrifuge and add a few drops of  $\text{AgNO}_3$  solution to the clear centrifugate: a white precipitate, soluble in dilute  $\text{NH}_3$  solution and reprecipitated by dilute  $\text{HNO}_3$ , indicates chloride.

**6. Chloride in the presence of Iodide (Bromide being absent).**—Add excess of  $\text{AgNO}_3$  solution to 0.5 ml. of the " $\text{Na}_2\text{CO}_3$  prepared solution" acidified with dilute  $\text{HNO}_3$ : centrifuge and reject the centrifugate. Wash the precipitate with about 0.2 ml. of dilute  $\text{NH}_3$  solution and centrifuge again. Acidify the clear washings with dilute  $\text{HNO}_3$ : a white precipitate ( $\text{AgCl}$ ) indicates the presence of chloride.

**7. Chloride in the presence of Bromide (Iodide being absent).**—Acidify 0.5 ml. of the " $\text{Na}_2\text{CO}_3$  prepared solution" contained in a semimicro boiling tube with dilute  $\text{HNO}_3$ , and add an equal volume of concentrated  $\text{HNO}_3$ . Boil gently until all the bromine is expelled, and then add  $\text{AgNO}_3$  solution. A white precipitate ( $\text{AgCl}$ ) indicates chloride present.

**8. Bromide and Iodide in the presence of each other.**—Dissolve 10–20 mg. of the mixture in 0.5–1 ml. of water, add 5 drops of dilute  $\text{H}_2\text{SO}_4$  and 0.3–0.5 ml. of  $\text{CCl}_4$ : or use 0.3 ml. of the " $\text{Na}_2\text{CO}_3$  prepared solution" acidified with dilute  $\text{H}_2\text{SO}_4$ , add 5 drops of dilute  $\text{H}_2\text{SO}_4$  and 0.5 ml. of  $\text{CCl}_4$ . Then introduce dilute  $\text{NaOCl}$  solution dropwise, shaking after the addition of each drop. A violet coloration of the  $\text{CCl}_4$  layer, which appears first, indicates iodide: this subsequently disappears and is replaced by a reddish-brown (or brown) coloration if a bromide is present.

**9. Thiocyanate, Chloride, Bromide and Iodide in the presence of each other.**—This problem may arise in the tests with  $\text{AgNO}_3$  solution (see Section VI, 5, test 4) since  $\text{AgSCN}$ ,  $\text{AgCl}$ ,  $\text{AgBr}$  and  $\text{AgI}$  are precipitated in *ca. N*  $\text{HNO}_3$  solution: interfering anions (*e.g.*  $\text{IO}_3^-$  which reacts with  $\text{SCN}^-$ ) are assumed to be absent. The precipitate may be formed, for example, from 0.5 ml. of the " $\text{Na}_2\text{CO}_3$  prepared solution" and is collected, after centrifuging, in a semimicro centrifuge or test-tube. Add 5–10 drops of water, stir the suspension and transfer three-quarters of it by means of a capillary pipette to a small crucible; this portion will be used in the tests for  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ , and the remainder for  $\text{SCN}^-$ .

**Thiocyanate test.**—Treat one-quarter of the precipitate with 5–10 drops of 5 per cent  $\text{NaCl}$  solution, heat and stir in

the hot water rack for 3–5 minutes (this converts part of the  $\text{AgSCN}$  into  $\text{NaSCN}$ ). Centrifuge and add to the clear centrifugate one drop of dilute  $\text{HCl}$  and one drop of  $\text{FeCl}_3$  solution. A red coloration indicates *thiocyanate present*.

If thiocyanate is present, it must be destroyed since it interferes with the tests for the halides. Dry the main precipitate in the crucible by heating gently in an air bath (Fig. II, 3, 16), remove the air bath and heat directly to dull redness for one minute or until all the thiocyanate is decomposed, *i.e.* until blackening of the precipitate and/or burning of sulphur just ceases. Prolonged heating should be avoided. Allow to cool.

Mixtures of halides may now be identified as indicated in 5–8 above: a systematic procedure, which covers the three halides, is given below.

To the residue in the crucible (if thiocyanate is present) or to the remainder of the precipitate transferred to a 5 or 10 ml. beaker (if thiocyanate is absent), add 100–150 mg. of zinc powder (20 mesh) and 10–15 drops of dilute  $\text{H}_2\text{SO}_4$ . Allow the reduction to proceed for 5–10 minutes with intermittent stirring: *gentle* warming for a few seconds may be necessary to start the reaction. Transfer the liquid, with the aid of a few drops of dilute  $\text{H}_2\text{SO}_4$ , to a centrifuge tube, centrifuge and divide the clear centrifugate into three equal parts.

**Iodide test.** Add 4–5 drops of  $\text{CCl}_4$  and 5 drops of 3 per cent  $\text{H}_2\text{O}_2$  or 5 drops of 25 per cent  $\text{Fe}_2(\text{SO}_4)_3$  solution. Agitate vigorously and allow to settle. Purple to violet colour of the  $\text{CCl}_4$  layer. *Iodide present*.

**Bromide test.** (a) If iodide is present, it must be removed by treating one-third of the solution with 5 drops of dilute  $\text{H}_2\text{SO}_4$  and 2 drops of 30 per cent  $\text{NaNO}_2$  solution (chloride-free). Boil down gently to 3–4 drops and allow to cool. Transfer the solution to a centrifuge tube and test for bromide as under (b).

(b) If iodide is absent, use one-third of the solution directly. Add an equal volume of concentrated  $\text{HNO}_3$ , heat in the boiling water bath for 30 seconds, and cool to room temperature with cold water. Add 3–4 drops of  $\text{CCl}_4$  and stir vigorously with a glass rod. A brown colour in the  $\text{CCl}_4$  layer indicates *bromide present*.

**Chloride test.** (a) If iodide and/or bromide present, dilute the remaining third of the solution to 0.5 ml., add 1 ml. of concentrated  $\text{HNO}_3$  and boil gently until evolution of bromine ceases. Cool, dilute and test for chloride as in (b) below with  $\text{AgNO}_3$  solution only.

(b) If bromide and iodide are absent, add 2 drops each of dilute  $\text{HNO}_3$  and  $\text{AgNO}_3$  solution. A white precipitate ( $\text{AgCl}$ ) indicates *chloride present*.

**10. Phosphate, Arsenate and Arsenite in the presence of each other.**—This problem may arise in the test with  $\text{AgNO}_3$  in neutral solution (see Section VI, 5, test 4).



Dilute 5 drops of the " $\text{Na}_2\text{CO}_3$  prepared solution" with an equal volume of water, acidify with dilute  $\text{HCl}$  and render alkaline with dilute  $\text{NH}_3$  solution. Centrifuge, if necessary, and discard the ppt. Treat the clear solution with 10–12 drops of  $\text{Mg}(\text{NO}_3)_2$  reagent (or of magnesia mixture) added dropwise and with stirring. Allow to stand for 10 minutes, stirring frequently; centrifuge. Wash the ppt. with 2–3 drops of dilute  $\text{NH}_3$  solution.

**Residue.** May contain  $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{Mg}(\text{NH}_4)\text{AsO}_4 \cdot 6\text{H}_2\text{O}$  (A).

Dissolve the ppt. in 5–10 drops of dilute  $\text{HCl}$ , add 1 drop of 10%  $\text{NH}_4\text{I}$  solution, heat to boiling and saturate with  $\text{H}_2\text{S}$  (Fig. II, 3, 17). Centrifuge, and saturate again with  $\text{H}_2\text{S}$  to ensure complete precipitation. Wash with a few drops of 0.5N  $\text{HCl}$ .

**Residue.**  
 $\text{As}_2\text{S}_3$ —  
yellow.  
**Arsenate**  
**present.**

**Centrifugate.** Transfer to a small crucible, boil until  $\text{H}_2\text{S}$  is expelled and volume is reduced to 2–3 drops. Transfer, with the aid of a few drops of water, to a centrifuge tube, make alkaline with dilute  $\text{NH}_3$  solution and add 5 drops in excess. Add 10 drops of  $\text{Mg}(\text{NO}_3)_2$  reagent (or of magnesia mixture), and allow to stand, with frequent stirring, for 10 minutes.

White ppt. of  $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$ .

**Phosphate present.**

**Centrifugate.** May contain arsenite.

Add 6–8 drops of 3%  $\text{H}_2\text{O}_2$  solution (to oxidise arsenite to arsenate), heat on water bath for 1 minute, cool, add 5–10 drops of  $\text{Mg}(\text{NO}_3)_2$  reagent (or of magnesia mixture), and allow to stand for 5–10 minutes, stirring frequently.

White ppt. of  $\text{Mg}(\text{NH}_4)\text{AsO}_4 \cdot 6\text{H}_2\text{O}$ .

**Arsenite present.**

Alternatively, acidify with dilute  $\text{HCl}$  and pass  $\text{H}_2\text{S}$ . Immediate yellow ppt. of  $\text{As}_2\text{S}_3$ .

**Arsenite present.**

*Note.* The presence of arsenate is readily detected as follows. Treat a portion of the ppt. A with 5 drops of  $\text{AgNO}_3$  solution to which 1 drop of 3N acetic acid has been added. If the ppt. acquires a reddish colour (due to  $\text{Ag}_3\text{AsO}_4$ ), arsenate is present. The yellow colour of  $\text{Ag}_3\text{PO}_4$  is obscured by the red colour of  $\text{Ag}_3\text{AsO}_4$ .

## VI, 8. EXAMINATION FOR METAL IONS (CATIONS) IN SOLUTION

**Preparation of a solution of the solid.**—Since the whole scheme for the analysis of cations depends upon the reactions of ions, it is clear that it is first necessary to get the substance into solution. Water is first tried in the cold and then on

warming. If insoluble in water, the following reagents are investigated as solvents in the order indicated: dilute hydrochloric acid, concentrated hydrochloric acid, dilute nitric acid, concentrated nitric acid and aqua regia (3 volumes of concentrated HCl to 1 volume of concentrated  $\text{HNO}_3$ ). Most substances encountered in an elementary course will dissolve in either water or dilute hydrochloric acid. If concentrated hydrochloric acid has to be used, the solution must be considerably diluted before proceeding with the analysis, otherwise certain cations, such as cadmium and lead, will not be precipitated by hydrogen sulphide. When concentrated nitric acid or aqua regia is employed as the solvent, the solution must be evaporated almost to dryness, a little hydrochloric acid added, the solution evaporated again to small bulk and then diluted with water to dissolve the soluble nitrates (or chlorides). This evaporation is necessary because the nitric acid may react with the hydrogen sulphide subsequently employed in the Group analysis.

To discover the most suitable solvent, treat portions of about 15 mg.\* of the finely powdered substance successively with 0.3–0.5 ml. of (1) water, (2) dilute hydrochloric acid, (3) concentrated hydrochloric acid, (4) dilute nitric acid, (5) concentrated nitric acid and (6) aqua regia (3 volumes of concentrated HCl : 1 volume of concentrated  $\text{HNO}_3$ ) in the order given. Try the solubility first in the cold and then at the temperature of a boiling water bath for water and dilute hydrochloric acid using a semimicro test-tube. For the other solvents, it will be necessary to investigate the solubility in a semimicro boiling tube; if solution does not take place in the cold, warm gently with a semimicro burner. When all the substance has dissolved, transfer to a semimicro test-tube, rinse the boiling tube with a few drops of water, and add the “rinsings” to the solution. If you are in doubt as to whether the substance or a portion of the substance has dissolved, evaporate a little of the clear solution on a watch glass.

If the substance dissolves in water, proceed immediately to the test for the metal ions. If the use of dilute hydrochloric acid results in the formation of a precipitate, this may consist of the metals of Group I; the precipitate may either be filtered off and examined for this Group, or else the original substance may be dissolved in dilute nitric acid. If concentrated acids are employed for dissolution, the remarks in the first paragraph must be borne in mind.

\* This is most simply estimated by weighing out 75 mg. and dividing it into 5 approximately equal parts.

**Oxides, Hydroxides, Free Metals and Simple Alloys.—**

If a solid substance is found to contain no anions, it may be an oxide, or hydroxide, or a metal or a mixture of metals, or an alloy. Metals and alloys have certain characteristic physical properties; many metals evolve hydrogen on treatment with dilute acids. As a rule, nitric acid must be employed as solvent, and it will then be necessary to remove the excess of nitric acid (as already described above) before proceeding to the Group analysis.

When a suitable solvent has been found, prepare the solution for analysis using about 50 mg. of the solid: the volume of the final solution should be 1–1.5 ml. Use this solution for the Separation of Cations into Groups according to Table SM.S (Section VI, 9). The various precipitates are investigated by means of the appropriate Group Separation Tables SMI–SMVII, given in Chapter III.

NOTES ON TABLE SM.S (SIMPLIFIED GENERAL TABLE FOR  
SEPARATION OF CATIONS INTO GROUPS)

(1) For the sake of uniformity throughout the text, a drop is intended to mean 0.05 ml.—the volume of the drop delivered by the commercial “medicine dropper.” If the instructions require the addition of 0.5 ml., this quantity can be measured out with the aid of a small measuring cylinder or graduated pipette, or 10 drops can be added directly from a reagent dropper provided, of course, that a drop from the latter does not differ appreciably from 0.05 ml. It is recommended that all droppers be calibrated (see Table SMI, Note 1; Section III, 5) and a small label, stating the number of drops per ml., attached to the upper part.

(2) The student must remember that in all operations with the centrifuge, the tube must be counterbalanced with another similar tube containing the same volume of water.

If the substance was completely soluble in dilute HCl, it is evident that no silver or mercurous salt is present. When lead is present, the solution may be clear while hot, but  $\text{PbCl}_2$  is deposited on cooling the solution, due to the slight solubility of this salt in cold water. Lead may be found in Group II, even if it is not precipitated in Group I.

(3) It is usually advisable in Group Separations to wash a precipitate with a small volume of a suitable wash solution and to add the washings to the centrifugate. In the present instance cold water or cold, very dilute HCl (say, *ca.* 0.5*N*) may be used. The precipitating reagent, diluted 10–100-fold, is generally a suitable wash liquid. Specific directions for washing precipitates will usually be omitted from the present Table in order to economise space.

## VI, 9.

## Table SM.S.—Separation of Cations into Groups

(Organic Acids, Boric, Hydrofluoric, Silicic and Phosphoric Acids being absent)

Add 2 drops (1) of dilute HCl to 1 ml. of the clear solution in a 3 ml. centrifuge tube (or a 4 ml. test-tube). If a ppt. forms, stir and add a further 1-2 drops to ensure complete precipitation. Centrifuge (2); wash the ppt. with a few drops of cold water (3) and add washings to centrifuge.	
<b>Residue.</b> The ppt. may contain: PbCl <sub>2</sub> —white. Hg <sub>2</sub> Cl <sub>2</sub> —white. AgCl—white. Bi <sub>2</sub> S <sub>3</sub> —black or black or CuS—black. CdS—yellow. SnS <sub>2</sub> —yellow. Sb <sub>2</sub> S <sub>3</sub> —yellow. As <sub>2</sub> S <sub>3</sub> —orange. Yellow.	<b>Centrifugate.</b> This must not give a ppt. with 1 drop of dilute HCl. Add 4 drops of 3% H <sub>2</sub> O <sub>2</sub> solution (4), and heat on a water bath for 2-3 minutes. Adjust the HCl concentration to about 0.3N (5). Pass H <sub>2</sub> S through the warm solution until precipitation is complete (6). Centrifuge and wash (7).
<b>Group I (Silver Group) present.</b> Examine by Group Separation Table SMI (Section III, 5).	<b>Residue.</b> The ppt. may contain: Fe(OH) <sub>3</sub> —reddish-brown. Cr(OH) <sub>3</sub> —green. Al(OH) <sub>3</sub> —white. MnO <sub>2</sub> ·xH <sub>2</sub> O—brown. <b>Group IIIA (Iron Group) present.</b> Examine by Group Separation Tables SMIV and SMVIA (Sections III, 10 and III, 18).
<b>Groups IIA and IIB (Copper and Arsenic Groups) present.</b> Examine by Group Separation Tables SMIIA and SMIIIA (Sections III, 10 and III, 18).	<b>Centrifugate.</b> Add 1-2 drops of dilute NH <sub>3</sub> solution, warm and pass H <sub>2</sub> S for 1 minute. Centrifuge (10) and wash (11). <b>Residue.</b> The ppt. may contain: CoS—black. NiS—black. MnS—pink. ZnS—white. <b>Group IIIB (Zinc Group) present.</b> Examine by Group Separation Table SMV (Section III, 28).
<b>Groups IIA and IIB (Copper and Arsenic Groups) present.</b> Examine by Group Separation Tables SMIIA and SMIIIA (Sections III, 10 and III, 18).	<b>Centrifugate.</b> This must give no further ppt. with H <sub>2</sub> S (10). Transfer to a small crucible and acidify with dilute acetic acid (12). Evaporate to a pasty mass [FUME CUPBOARD], allow to cool, add 5-10 drops of concentrated HNO <sub>3</sub> so as to wash down to the centre of the crucible most of the solid adhering to the walls. Heat cautiously until dry and then more strongly until white fumes cease to be evolved (13). Cool. Add 5 drops of dilute HCl and 0.5 ml. of water, warm and stir; transfer the solution with the aid of 0.5 ml. of water, to a 3 ml. centrifuge tube. If the solution is not clear, centrifuge and remove the clear solution to another tube. Add 25 mg. of solid NH <sub>4</sub> Cl (or 0.25 ml. of 10% NH <sub>4</sub> Cl solution), render alkaline with concentrated NH <sub>3</sub> solution, and then add, with stirring, 0.3 ml. of (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> solution. Keep and stir the mixture in a water bath at 50-60°C (14) for 2-3 minutes. Centrifuge and wash with a few drops of hot water.
<b>Groups IIA and IIB (Copper and Arsenic Groups) present.</b> Examine by Group Separation Tables SMIIA and SMIIIA (Sections III, 10 and III, 18).	<b>Residue.</b> The ppt. may contain: BaCO <sub>3</sub> —white. SrCO <sub>3</sub> —white. CaCO <sub>3</sub> —white. <b>Group IV (Calcium Group) present.</b> Examine by Group Separation Table SMVI or SMVIA (Section III, 32).
<b>Groups IIA and IIB (Copper and Arsenic Groups) present.</b> Examine by Group Separation Tables SMIIA and SMIIIA (Sections III, 10 and III, 18).	<b>Centrifugate.</b> May contain Mg <sup>++</sup> , Na <sup>+</sup> and K <sup>+</sup> (15). Evaporate to a pasty mass in a porcelain crucible [FUME CUPBOARD], add 0.5 ml. of concentrated HNO <sub>3</sub> , evaporate cautiously to dryness and then heat until no more white fumes are evolved. White residue. <b>Group V (Alkali Group) present.</b> Examine by Group Separation Table SMVII (Section III, 37).

Note. In Group Separation Tables SMI, SMIV, SMV, SMVI and SMVIA, commence at the point marked (T).

(4) The  $\text{H}_2\text{O}_2$  solution is added to oxidise  $\text{Sn}^{++}$  to  $\text{Sn}^{+++}$ , thus leading ultimately to the precipitation of  $\text{SnS}_2$  instead of the somewhat gelatinous  $\text{SnS}$ . The excess of  $\text{H}_2\text{O}_2$  should preferably be decomposed by boiling before passing  $\text{H}_2\text{S}$ , otherwise some S may be precipitated; the latter may mislead the unwary student if Group II elements are absent. The subsequent separation of Groups IIA and IIB by means of aqueous KOH is thus rendered more complete since  $\text{SnS}_2$  dissolves completely and  $\text{SnS}$  dissolves only partially in aqueous KOH.

If it is intended to use ammonium polysulphide in the separation of Groups IIA and IIB (by an adaptation of Table III, Section III, 18), the addition of  $\text{H}_2\text{O}_2$  is not essential since  $(\text{NH}_4)_2\text{S}_x$  will oxidise the  $\text{SnS}$  to  $\text{SnS}_2$  and the latter dissolves as the thiostannate  $(\text{NH}_4)_2\text{SnS}_3$ .

(5) It is important that the concentration of HCl be approximately correct, *i.e.* 0.3*M*, before passing  $\text{H}_2\text{S}$ : with higher concentrations of acid, lead, cadmium and stannous tin will be incompletely precipitated: if the acidity is too low, sulphides of Group IIIB (NiS, CoS and ZnS) may be precipitated. Either of two methods may be employed to adjust the acid concentration.

(a) Run in exactly 5.0 ml. of distilled water from a burette, etc., into a clean, dry conical flask of 10 ml. capacity: attach a label to the latter so that the upper edge of the label is in line with the level of the water. Pour out the water.

Transfer the centrifugate from Group I to the calibrated 10 ml. conical flask with the aid of a few drops of water. Add concentrated  $\text{NH}_3$  solution dropwise (use a capillary dropper) with constant stirring, until the mixture is alkaline. [Ignore any precipitate which may form: this will dissolve when HCl is added or will be converted by the  $\text{H}_2\text{S}$  treatment into the sulphide.] Then add dilute HCl by means of a capillary dropper, with constant stirring, until the mixture is *just* acid (test with litmus paper by removing a drop with a micro stirring rod). Now add exactly 0.50 ml. of 3*N* HCl (measured from a calibrated dropper or from a 1 ml. graduated pipette), and dilute the solution with distilled water to the 5 ml. mark.

(b) A simple procedure is to use the indicator methyl violet (0.1 per cent aqueous solution or, better, the purchased or prepared indicator paper). The following table gives the colour of the indicator at various concentrations of acid.

<i>Acid concentration</i>	<i>pH</i>	<i>Methyl violet indicator</i>
Neutral or alkaline	7+	Violet.
0.1 <i>N</i> HCl	1.0	Blue.
0.25 <i>N</i> HCl	0.6	Blue-green.
0.33 <i>N</i> HCl	0.5	Yellow-green.
0.50 <i>N</i> HCl	0.3	Yellow.

Add 1 micro drop of methyl violet indicator solution and introduce dilute  $\text{NH}_3$  solution with constant stirring until the colour of the solution is yellow-green. A blue-green colour is almost but not quite acid enough.

find detection of slight colour changes difficult may, indeed, prefer the blue-green colour change. If the indicator paper is available, the thoroughly stirred solution should be spotted with a micro stirring rod on fresh portions of the paper. It is recommended that a comparison solution containing, say, 2 ml. of 0.3*N* HCl and 1 micro drop of indicator be freshly prepared: this will facilitate the correct adjustment of the acidity. A more satisfactory standard is a buffer solution prepared by mixing 1 ml. of *N* sodium acetate and 2 ml. of *N* HCl: this has a pH of 0.5.

(6) For the passage of  $\text{H}_2\text{S}$  into the solution, the "pressure" method detailed in Section II, 2, 7 (see also Section II, 3, 12) should be employed. The solution, contained in a 10 ml. conical flask or in a 4 ml. test-tube, is heated (the former directly on a wire gauze, the latter in a hot water bath), a capillary delivery tube is inserted and  $\text{H}_2\text{S}$  passed in, whilst slowly shaking the vessel with a swirling motion until precipitation is complete: the latter will be apparent when bubbling either stops altogether or is reduced to a very slow rate of 1-2 bubbles per minute. Saturation is normally complete in 1-2 minutes. The best method of determining whether precipitation is complete is to centrifuge a portion of the solution and to test the centrifugate with  $\text{H}_2\text{S}$ . If only a white precipitate or a suspension of sulphur is obtained, the presence of an oxidising agent is indicated.

If an oxidising agent is present (e.g. a permanganate, dichromate or a ferric salt) as is shown by the gradual separation of a fine white precipitate of sulphur and/or a change in colour of the solution, it is usual to pass  $\text{SO}_2$  into the hot solution until reduction is complete, then to boil off the excess of  $\text{SO}_2$  (conical flask or small beaker or crucible; test with  $\text{K}_2\text{Cr}_2\text{O}_7$  paper), and finally to pass  $\text{H}_2\text{S}$ . Arsenates, in particular, are slowly precipitated by  $\text{H}_2\text{S}$ : they are therefore usually reduced by  $\text{SO}_2$  to arsenites and then precipitated as  $\text{As}_2\text{S}_3$  with  $\text{H}_2\text{S}$ , after removal of the excess of  $\text{SO}_2$  in order to avoid interaction of the latter with  $\text{H}_2\text{S}$  and consequent separation of S. Stannic compounds may be very slightly reduced to the stannous state by this treatment; the amount of reduction is, however, so small that it may be neglected. The original solution or substance must be tested for the valence state of the arsenic.

The objection to the use of  $\text{SO}_2$  is that some sulphuric acid may be formed, especially on boiling, and this may partially precipitate Pb, Sr and Ba as sulphates. Any precipitate formed in this process should therefore be examined for these cations:  $\text{PbSO}_4$  is soluble in ammonium acetate solution.

An alternative procedure to be used when arsenate is present, which does not possess the disadvantages associated with  $\text{SO}_2$  and is perhaps more expeditious, is to add 0.2 ml. of concentrated HCl and 2 drops of 10 per cent  $\text{NH}_4\text{I}$  solution: the arsenate is thereby reduced to arsenite and upon saturation of the warm solution with  $\text{H}_2\text{S}$  under "pressure," the arsenic is completely precipitated as

$\text{As}_2\text{S}_3$ . This reduction may be carried out after the sulphides of the other elements have been precipitated in the presence of 0.3N HCl.

(7) The wash liquid is prepared by dissolving 0.1 gram of  $\text{NH}_4\text{NO}_3$  in 2 ml. of water and treating this solution with  $\text{H}_2\text{S}$ : about 0.2 ml. will suffice for the washing. The  $\text{H}_2\text{S}$  must be present in the wash liquid to prevent oxidation of the moist sulphides to sulphates.

(8) If iron was originally present in the ferric state, it will be reduced to the ferrous condition by  $\text{H}_2\text{S}$ . It must be oxidised to the ferric condition with concentrated nitric acid (or with a few drops of saturated bromine water) to ensure complete precipitation with  $\text{NH}_4\text{Cl}$  and dilute  $\text{NH}_3$  solution. The original solution must be tested to determine whether the iron is present as  $\text{Fe}^{++}$  or as  $\text{Fe}^{+++}$ .

The nitric acid will simultaneously oxidise any HI, if  $\text{NH}_4\text{I}$  has been used to reduce arsenates, etc.

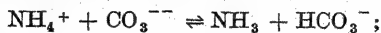
(9) The washing may be made with a little hot water or, better, 2 per cent  $\text{NH}_4\text{NO}_3$  solution.

(10) If the centrifugate is brown or dark-coloured, Ni may be suspected. The dark-coloured solution contains colloidal NiS, which centrifuges with difficulty. It may be acidified with dilute acetic acid and boiled (crucible or semimicro boiling tube) until the NiS has coagulated: this may be added to the Group IIIB precipitate or tested separately for Ni.

(11) The wash liquid may consist of 1 per cent  $\text{NH}_4\text{Cl}$  solution to which 1 per cent by volume of ammonium sulphide solution has been added. Oxidation of the moist sulphides to sulphates is thus reduced considerably.

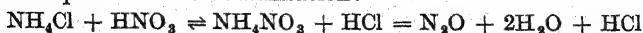
(12) The filtrate must be acidified immediately and concentrated to remove  $\text{H}_2\text{S}$ . Ammonium sulphide solution upon exposure to air slowly oxidises to ammonium sulphate and would then precipitate any Ba or Sr present as  $\text{BaSO}_4$  or  $\text{SrSO}_4$ . Another reason for acidifying the filtrate from Group IIIB is to prevent absorption of  $\text{CO}_2$  from the air with the formation of carbonate ions: the latter would also precipitate the ions of Group IV.

(13) The initial centrifugate from Group IIIB will be almost saturated with ammonium salts and this concentration of ammonium ions is higher than is necessary to prevent the precipitation of  $\text{Mg}(\text{OH})_2$  and it may also lead to incomplete precipitation of the carbonates of Group IV. The latter effect is due to the acidic properties of the ammonium ion:



the concentration of  $\text{CO}_3^{--}$  ions upon the addition of  $(\text{NH}_4)_2\text{CO}_3$  would thus be considerably reduced. For these reasons most of the ammonium salts must be eliminated first.

Concentrated  $\text{HNO}_3$  decomposes  $\text{NH}_4\text{Cl}$  at a lower temperature than is required for its volatilisation:



Loss by decrepitation and spitting during these operations must be avoided.

(14) Ammonium carbonate decomposes appreciably above 60°C



The digestion also improves the filtering properties of the precipitate.

(15) Owing to the slight solubility of  $\text{CaCO}_3$ ,  $\text{SrCO}_3$  and  $\text{BaCO}_3$  in solutions of ammonium salts, the centrifugate from Group IV will, when these metals are present, contain minute amounts of the ions of the alkaline earth metals. Since the Group IV metals may interfere to a limited extent with the flame tests for Na and K and also the  $\text{Na}_2\text{HPO}_4$  test for Mg (if employed), it has been recommended that the filtrate from Group IV be heated on a water bath for 2–3 minutes with half a drop each of  $(\text{NH}_4)_2\text{SO}_4$  solution and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution; any precipitate which forms is removed by centrifugation and discarded. Owing to the comparatively small concentration of ammonium salts, this is generally unnecessary if the procedure described in Table SMVII (Section III, 37) is adopted.

**VI, 10. Modification of the analysis in the presence of Phosphate, etc.**—With the experience gained in the foregoing comparatively elementary analysis, the student should have no serious difficulty in adapting the macro procedures of the more advanced analysis described in Chapters VII, VIII and IX to the semimicro scale. As an example, we may take the Phosphate Separation Table (compare Table II in Section VII, 7 and Table P in Section V, 10). This is given in Table SMVIII below.

A brief mention may be made here concerning **the removal of certain other interfering ions**. This should be effected *before* the phosphate separation.

If borate is found to be present, transfer the centrifugate from Group II to a small crucible, heat to expel hydrogen sulphide (do not evaporate to dryness), and allow to cool. Add 2–3 drops of concentrated hydrochloric acid and 5–6 drops of methyl alcohol, and heat on a water bath until the solution is almost evaporated to dryness. Repeat the addition of hydrochloric acid and methyl alcohol, and evaporate to dryness on the water bath. If borate is the only interfering ion, dissolve the residue in 2 ml. of 0.3*N* hydrochloric acid, and continue the analysis for cations. The borate is volatilised as methyl borate (*poisonous*).

If **oxalate or acetate** is found to be present, add to the residue from which borate has been removed (or, if borate is absent, the centrifugate from Group II which has been evaporated almost to dryness) 1 ml. of concentrated hydrochloric



## VI, 10. Table SMVIII.—Phosphate Separation Table

Place the centrifugate from Group II in a semimicro boiling tube (or small crucible), boil to expel  $\text{H}_2\text{S}$ , add 1–2 drops of concentrated  $\text{HNO}_3$  (or 5–10 drops of bromine water) and boil gently for 1 minute. Transfer to a 4 ml. test-tube with the aid of 0.5 ml. of water. Add 1 drop of  $\text{NH}_4\text{Cl}$  solution and 2–3 drops of the zirconium nitrate reagent, warm on water bath for 2 minutes and centrifuge. Test for completeness of precipitation by adding a further drop of the zirconium nitrate reagent to the centrifugate: if a ppt. forms, centrifuge again and repeat the process until the addition of 1 drop of the reagent to the clear centrifugate has no visible effect. Heat on a boiling water bath, with stirring, for 1 minute; centrifuge. Wash with a few drops of hot water.

**Residue.**  
Zirconium  
phosphate.  
Reject.

**Centrifugate.** Add 50 mg. of solid  $\text{NH}_4\text{Cl}$  (or 0.25 ml. of 20%  $\text{NH}_4\text{Cl}$  solution), heat on a water bath, add concentrated  $\text{NH}_3$  solution until alkaline and then 2 drops in excess. Place the tube in the boiling water bath for 3–5 minutes. Centrifuge. Wash with a few drops of hot water or 2%  $\text{NH}_4\text{NO}_3$  solution.

**Residue.** Examine for Group IIIA. The excess of Zr will be found in the residue after treatment with  $\text{H}_2\text{O}_2$  and  $\text{NaOH}$  solution (or with sodium perborate  $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$  and boiling), and will accompany any  $\text{Fe}(\text{OH})_3$ , if Fe is present.

**Centrifugate.**  
Examine for  
Groups IIIB,  
IV and V.

acid and 0.5 ml. of concentrated nitric acid. Evaporate slowly almost to dryness: use a crucible. Allow to cool, then add 1 ml. of concentrated hydrochloric acid and 1 ml. of concentrated nitric acid, and evaporate just to dryness. Dissolve the residue in 2 ml. of 0.3*N* hydrochloric acid and continue the analysis for cations. The evaporation with  $\text{HCl}$ – $\text{HNO}_3$  mixture will destroy the organic acids and simultaneously remove any fluoride which may be present.

## VI, 11. ANALYSIS OF A LIQUID (SOLUTION)

If a liquid is supplied for analysis, proceed as follows:

(1) Observe the colour, odour and any special physical properties.

(2) Test its reaction to litmus (or equivalent test) paper.

(a) *The solution is neutral*: free acids, free bases, acid salts, and salts which give an acid or alkaline reaction owing to hydrolysis, are absent.

- (b) *The solution reacts alkaline*: this may be due to the hydroxides of the alkali and alkaline earth metals, to the carbonates, sulphides, hypochlorites and peroxides of the alkali metals, etc.
- (c) *The solution reacts acid*: this may be due to free acids, acid salts, salts which yield an acid reaction because of hydrolysis, or to a solution of salts in acids.

(3) Evaporate a portion of the liquid to dryness on the water bath (use a 5 or 8 ml. crucible and stand it over one of the openings in the hot water rack); carefully smell the vapours evolved from time to time. If a solid residue remains, examine it as detailed above for a solid substance. If a liquid remains, evaporate cautiously on a wire gauze in the fume chamber; a solid residue should then be examined in the usual way. If no residue is obtained, the original liquid consists of some volatile substances which may be water or water containing certain gases or volatile substances, such as  $\text{CO}_2$ ,  $\text{NH}_3$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{H}_2\text{O}_2$  or  $(\text{NH}_4)_2\text{CO}_3$ , all of which can be readily detected by special tests. It is best to neutralise with sodium carbonate and test for acid radicals (anions).

## CHAPTER VII

### SYSTEMATIC QUALITATIVE INORGANIC ANALYSIS

In the scheme of analysis to be described in the following pages, it is assumed that the student is already familiar with the tests and operations described in the preceding chapters. It will be shown how these isolated facts are incorporated in the systematic methods of qualitative analysis, applicable not only to simple solid substances, but also to mixtures of solid substances, to liquids, to alloys, and to "insoluble" substances, *i.e.* substances which are insoluble in aqua regia and acid solvents.

It must be emphasised that the object of qualitative analysis is not simply to detect the constituents of a given mixture; an equally important aim is to ascertain the approximate relative amounts of each component. For this purpose 0.5–1 gram of the substance is usually employed for the analysis; the relative magnitudes of the various precipitates will provide a rough guide as to the proportions of the constituents present.

Every analysis is divided into three parts:

(1) *The preliminary examination.* This includes preliminary examination by dry tests, examination of the volatile products with sodium hydroxide solution (for ammonium), and with dilute and concentrated sulphuric acid (for acid radicals or anions).

(2) *The examination for metal ions (cations) in solution.*

(3) *The examination for acid radicals (or anions) in solution.*

The substance to be analysed may be: (A) *solid and non-metallic*, (B) *a liquid (solution)*, (C) *a metal or an alloy*, and (D) *an "insoluble" substance*. Each of these will be discussed separately.

#### VII, 1. ANALYSIS OF SOLID AND NON-METALLIC SUBSTANCES

The appearance of the substance should be carefully noted; a lens or microscope should be used, if necessary. Observe whether it is crystalline or amorphous, whether it is magnetic and whether it possesses any characteristic odour or colour.

Some of the commonly occurring coloured compounds are listed below:

*Red*:  $\text{Pb}_3\text{O}_4$ ,  $\text{As}_2\text{S}_2$ ,  $\text{HgO}$ ,  $\text{HgI}_2$ ,  $\text{HgS}$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{CrO}_3$ ,  $\text{Cu}_2\text{O}$ ,  $\text{K}_3[\text{Fe}(\text{CN})_6]$ ; dichromates are orange-red; permanganates and chrome alum are reddish-purple.

*Pink*: hydrated salts of manganese and of cobalt.

*Yellow*:  $\text{CdS}$ ,  $\text{As}_2\text{S}_3$ ,  $\text{SnS}_2$ ,  $\text{PbI}_2$ ,  $\text{HgO}$  (precipitated),  $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ ; normal chromates; ferric chloride and nitrate.

*Green*:  $\text{Cr}_2\text{O}_3$ ,  $\text{Hg}_2\text{I}_2$ ,  $\text{Cr}(\text{OH})_3$ ; ferrous salts, e.g.  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ; nickel salts;  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{CuCO}_3$ ,  $\text{K}_2\text{MnO}_4$ .

*Blue*: anhydrous cobalt salts; hydrated cupric salts; Prussian blue.

*Brown*:  $\text{PbO}_2$ ,  $\text{CdO}$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{Ag}_3\text{AsO}_4$ ,  $\text{SnS}$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}(\text{OH})_3$  (reddish-brown).

*Black*:  $\text{PbS}$ ,  $\text{CuS}$ ,  $\text{CuO}$ ,  $\text{HgS}$ ,  $\text{FeS}$ ,  $\text{MnO}_2$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{CoS}$ ,  $\text{NiS}$ ,  $\text{Ni}_2\text{O}_3$ ,  $\text{Ag}_2\text{S}$ ,  $\text{C}$ .

The colour of the solution obtained when the substance is dissolved in water or in dilute acids should be noted, as this may often give valuable information. The following colours are shown by the ions (the cations are usually hydrated) present in the dilute solution:

*Blue*: cupric copper; *green*: nickel, ferrous iron, chromic chromium, manganates; *yellow*: chromates, ferrocyanides, ferric iron; *orange-red*: dichromates; *purple*: permanganates; *pink*: cobalt, manganese.

The substance should be reduced to a fine powder in a suitable mortar before proceeding with the following tests. These tests usually give a great deal of useful information; they are quickly performed (10–15 minutes) and should never be omitted.

## VII, 2. PRELIMINARY DRY TESTS

The following tests are made:

(i) *action of heat*; (ii) *flame colorations*; (iii) *charcoal block reductions*; (iv) *borax and phosphate bead reactions*; (v) *ammonium radical test*.\*

**Test (i). Heating in a closed tube.**—Place a small quantity (4–5 mg.) of the substance in a dry ignition tube so that none of it remains adhering to the sides, and heat cautiously; the tube should be held in an almost horizontal position. The

\* This is really a wet test, but is included here for the sake of convenience.

temperature is gradually raised, and any changes which take place carefully noted.

Observation	Inference
<b>(a) The substance changes colour.</b> 1. Blackening from separation of carbon, often accompanied by burning. 2. Blackening, not accompanied by burning or odour. 3. Yellow when hot, white when cold. 4. Yellowish-brown when hot, yellow when cold. 5. Yellow when hot, yellow when cold. 6. Brown when hot, brown when cold. 7. Red to black when hot, brown when cold.	Organic substances, e.g. tartrates and citrates. Cu, Mn and Ni salts at a very high temperature. ZnO and many Zn salts. SnO <sub>2</sub> or Bi <sub>2</sub> O <sub>3</sub> . PbO and some Pb salts. CdO and many Cd salts. Fe <sub>2</sub> O <sub>3</sub> .
<b>(b) A sublimate is formed.</b> 1. White sublimate.* 2. Grey sublimate, easily rubbed to globules. 3. Steel-grey sublimate; garlic odour. 4. Yellow sublimate. 5. Blue-black sublimate; violet vapour. 6. Black; red on trituration.	HgCl <sub>2</sub> , HgBr <sub>2</sub> , Hg <sub>2</sub> Cl <sub>2</sub> , ammonium halides, As <sub>2</sub> O <sub>3</sub> , Sb <sub>2</sub> O <sub>3</sub> , certain volatile organic compounds (oxalic acid, benzoic acid). Hg. As. S (melts on heating), As <sub>2</sub> S <sub>3</sub> , HgI <sub>2</sub> (red when rubbed with a glass rod). I. HgS.
* If a white sublimate forms, heat with 4 times the bulk of anhydrous sodium carbonate and a little potassium cyanide in an ignition tube. A grey mirror, convertible into globules on rubbing with a glass rod, indicates Hg; a brownish-black mirror, yielding a white sublimate and an odour of garlic when heated in a wide tube, indicates As; ammonia evolved (test with mercurous nitrate paper) indicates ammonium salts.	
<b>(c) A gas or vapour is evolved.</b> 1. Water is evolved; test with litmus paper. The water is alkaline. The water is acid. 2. Oxygen is evolved (rekindles glowing splint). 3. Nitrous oxide (rekindles glowing splint) and steam are evolved.	Compounds with water of crystallisation (often accompanied by change of colour), ammonium salts, acid salts, oxy-acids, hydroxides. Ammonium salts. Readily decomposed salts of strong acids, also acids. Nitrates, chlorates, perchlorates, bromates, iodates, peroxides, per-salts and permanganates. Ammonium nitrate or nitrate mixed with an ammonium salt.

Observation	Inference
4. Dark-brown or reddish fumes (oxides of nitrogen); acidic in reaction.	Nitrates or nitrites of heavy metals.
5. Carbon dioxide is evolved (lime water rendered turbid).	Carbonates, bicarbonates, oxalates and organic compounds.
6. Carbon monoxide is evolved (burns with a blue flame forming carbon dioxide); <i>poisonous gas</i> .	Oxalates.
7. Cyanogen is evolved (burns with violet flame and characteristic odour); <i>very poisonous gas</i> .	Cyanides of heavy metals, <i>e.g.</i> of Hg and Ag; $K_3[Fe(CN)_6]$ .
8. Acetone is evolved (burns with luminous flame).	Acetates.
9. Ammonia is evolved (odour; turns red litmus paper blue; turns mercurous nitrate paper black).	Ammonium salts; certain complex amines.
10. Phosphine is evolved (odour of rotten fish; inflammable); <i>very poisonous</i> .	Phosphites and hypophosphites.
11. Sulphur dioxide is evolved (odour of burning sulphur; turns potassium dichromate paper green; decolourises fuchsin solution).	Normal and acid sulphites; thiosulphates; certain sulphates.
12. Hydrogen sulphide is evolved (odour of rotten eggs; turns lead acetate paper black or cadmium acetate paper yellow).	Acid sulphides; hydrated sulphides.
13. Chlorine is evolved (yellowish-green gas; bleaches litmus paper; turns potassium iodide-starch paper blue); <i>very poisonous</i> .	Unstable chlorides, <i>e.g.</i> of Cu, Au and Pt; chlorides in presence of oxidising agents.
14. Bromine is evolved (reddish-brown vapour; choking odour; turns fluorescein paper red).	Sources similar to chlorine.
15. Iodine is evolved (violet vapours condensing to black crystals).	Free iodine and certain iodides.

**Test (ii). Flame colorations.**—Place a small quantity (3–4 mg.) of the substance on a watch glass, moisten with a little concentrated hydrochloric acid, and introduce a little of the

Observation	Inference
Persistent golden-yellow flame.	Sodium.
Violet (lilac) flame.	Potassium.
Carmine-red flame.	Lithium.
Brick-red (yellowish-red) flame.	Calcium.
Crimson flame.	Strontium.
Yellowish-green flame.	Barium [molybdenum].
Green flame.	Borates, copper [thallium].
Livid blue flame (wire slowly corroded).	Lead, arsenic, antimony, bismuth, copper.

substance on a clean platinum wire into the base of the non-luminous Bunsen flame. An alternative method is to dip the platinum wire into concentrated hydrochloric acid contained in a watch glass and then into the substance; sufficient will adhere to the platinum wire for the test to be carried out.

The sodium flame masks that of other elements, *e.g.* that of potassium. Mixtures can be readily detected with the direct vision spectroscope (see Fig. II, 1, 4). A less delicate method is to view the flame through two thicknesses of cobalt blue glass, whereby the yellow colour due to sodium is masked or absorbed, and the other colours are modified as follows.

<i>Flame coloration</i>	<i>Flame coloration through cobalt glass</i>	<i>Inference</i>
Golden-yellow. Violet. Brick-red. Crimson. Yellowish-green.	Nil. Crimson. Light green. Purple. Bluish-green.	Sodium. Potassium. Calcium. Strontium. Barium.

### Test (iii). Charcoal block reductions.

(a) Heat a little of the substance (3–4 mg.) in a small cavity scooped in a charcoal block in a blowpipe flame.

<i>Observation</i>	<i>Inference</i>
1. The substance decrepitates.	Crystalline salts, <i>e.g.</i> NaCl, KCl.
2. The substance deflagrates.	Nitrates, nitrites, chlorates, perchlorates, iodates, permanganates.
3. The substance fuses and is absorbed by the charcoal, or forms a liquid bead.	Salts of the alkalis and some salts of the alkaline earths.
4. The substance is infusible and incandescent, or forms an incrustation upon the charcoal.	Apply test (b) below.

(b) Mix the substance (3–4 mg.) with twice its bulk of anhydrous sodium carbonate, place the mixture in a cavity of a piece of charcoal and heat in the reducing flame of the blowpipe.

The sodium carbonate converts a metallic salt into a carbonate or oxide on heating, and thus reduction occurs more rapidly than with the charcoal alone, as in (a). Further, the sodium carbonate acts as a flux and, in the fused state, protects any metallic globules, which may have formed beneath it, from oxidation.

Observation	Inference
1. White, infusible and incandescent when hot.	BaO, SrO, CaO, MgO (residue alkaline to litmus paper). Al <sub>2</sub> O <sub>3</sub> , ZnO, SiO <sub>2</sub> (residue not alkaline to litmus paper).
2. Incrustation without metal: White, yellow when hot. White, garlic odour. Brown.	ZnO. As <sub>2</sub> O <sub>3</sub> . CdO.
3. Incrustation with metal: White incrustation; brittle metal. Yellow incrustation; brittle metal. Yellow incrustation; malleable metal, marks paper.	Sb. Bi. Pb.
4. Metal without incrustation: Grey metallic particles, attracted by magnet. Malleable beads.	Fe, Ni, Co.  Ag and Sn (white), Cu (red flakes) [Au].

Sulphur compounds are reduced to sulphide by this treatment; the residue may be moistened with water and placed in contact with a silver coin when a brown to black stain of silver sulphide is obtained (*Hepar reaction*), or it may be extracted with a little water and filtered into a freshly prepared sodium nitroprusside solution, when an unstable purple coloration will indicate the presence of sulphur (see Section IV, 6, reaction 5).

(c) Moisten the substance or the infusible residue of test (b) with one to two drops of cobalt nitrate solution and ignite strongly.

Observation	Inference
1. Blue residue.	Al <sub>2</sub> O <sub>3</sub> , phosphates, arsenates, silicates, borates.
2. Green residue.	ZnO.
3. Pink residue.	MgO.

**Test (iv). Borax bead reactions.**—Prepare a borax bead in a loop of platinum wire by dipping the hot wire into borax and heating until colourless and transparent. Bring a *minute* quantity of the substance into contact with the hot bead and heat in the outer or oxidising flame. Observe the colour when the bead is hot and also when it is cold. Heat the bead in the inner or reducing flame and observe the colours in the hot and cold states. Coloured beads are obtained with compounds of copper, iron, chromium, manganese, cobalt and nickel (see, however, Section IX, 19, Table VI).



Oxidising flame	Reducing flame	Metal
1. Green when hot; blue when cold.	Colourless when hot, opaque-red when cold.	Copper.
2. Yellowish-brown or red when hot; yellow when cold.	Green, hot and cold.	Iron.
3. Dark yellow when hot, green when cold.	Green, hot and cold.	Chromium.
4. Violet (amethyst), hot and cold.	Colourless, hot and cold.	Manganese.
5. Blue, hot and cold.	Blue, hot and cold.	Cobalt.
6. Reddish-brown when cold.	Grey or black and opaque when cold.	Nickel.

The presence of manganese and of chromium is confirmed by fusing the substance with sodium carbonate and potassium nitrate on platinum foil or broken porcelain. A green mass on cooling indicates *manganese*; a yellow mass, *chromium*. The sodium carbonate bead test (Section II, 1, 7) may also be employed.

A useful reaction which may be carried out at this stage is the **microcosmic bead test** (Section II, 1, 6). This test is carried out in a loop of platinum wire exactly as for the borax bead test. The presence of a white skeleton (of silica) in the coloured glass indicates *silicate*. Stannic oxide  $\text{SnO}_2$  dissolves slowly in the bead and may be mistaken for silica.

**Test (v). Test for the ammonium radical.**—Boil a little (ca. 0.1 gram) of the substance with sodium hydroxide solution. The evolution of ammonia, detected by its odour and its action upon red litmus paper and upon filter paper soaked in mercurous nitrate solution,\* indicates the presence of an *ammonium salt*.

**Note.** Great care must be exercised when heating mixtures containing solutions of alkali hydroxides because of their destructive effects upon the eyes. These mixtures tend to bump and should preferably be heated in the fume cupboard. Under no circumstances should one attempt to smell the vapour whilst heating the mixture.

The following experimental details in testing for ammonia are of value for other gases (with suitable modification of reagents). In order to avoid holding the test paper (litmus, etc.) in the vapour, the apparatus shown in Fig. VII, 2, 1 may be employed; the test paper is supported on the upper end of the

\* Drop-reaction paper, treated with tannic acid and silver nitrate solution (see Section III, 36, reaction 7), may also be used.

wide glass tube. If ammonia is present, the litmus paper should show a gradual development of colour from the bottom upwards and should eventually become *uniformly* blue; scattered blue spots indicate that droplets of the alkaline solution have come into contact with the paper. The spray may be trapped, if desired, by a loosely fitting plug of cotton wool inserted in the upper part of the test-tube.

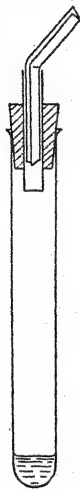


Fig. VII, 2, 1

If the evolved gas is soluble in water and a solution is required for further testing, the apparatus shown in Fig. IV, 2, 1 (with the delivery tube of fairly wide tubing and about twice the length of the test-tube or distilling flask in order to avoid the danger of "sucking back") may be employed. In the present case the ammonia may be absorbed in 3–4 ml. of distilled water. Upon adding Nessler's reagent (Section III, 36, 2—the second method of preparation is recommended), an orange or brown *precipitate* confirms ammonia. This test is an extremely sensitive one and in order to establish the presence of ammonia evolved in the reaction a precipitate and not a coloration must be obtained.

### VII, 3. PRELIMINARY TESTS FOR ACID RADICALS (ANIONS)

The action of dilute sulphuric acid (or of dilute hydrochloric acid) and of concentrated sulphuric acid upon the substance, combined with inferences drawn from the preliminary dry tests, supply much information which may be useful in the subsequent tests, notably for cations. Thus the presence of silicate, borate, fluoride, citrate, tartrate and possibly oxalate will have been indicated—phosphates are detected in the group separation after Group II; the course of systematic analysis for the metal ions can then be appropriately modified {see Table I (Section VII, 6), and discussion in Chapter VIII}. The indications of the preliminary tests must, of course, be confirmed. The systematic examination for acid radicals (anions) is usually carried out after that of the cations.

Before describing these preliminary tests, a summary of the solubilities of the salts of the more common acids in water may be found useful in the subsequent deductions.

*Nitrates, chlorates, acetates, manganates and permanganates* are all soluble; exceptions are a few basic nitrates (e.g. Bi and Sb) and basic acetates (e.g. Fe); silver and mercurous acetates are sparingly soluble.

*Nitrites* are all soluble; silver nitrite is sparingly soluble.

*Chlorides* are generally soluble; exceptions are  $\text{AgCl}$ ,  $\text{Hg}_2\text{Cl}_2$ ,  $\text{TiCl}_3$ ,  $\text{CuCl}$ ,  $\text{SbOCl}$ ,  $\text{BiOCl}$ , which are insoluble;  $\text{PbCl}_2$  is sparingly soluble.

*Bromides* have similar solubilities to the chlorides.

*Iodides* are generally soluble; exceptions are  $\text{AgI}$ ,  $\text{Hg}_2\text{I}_2$ ,  $\text{HgI}_2$ ,  $\text{CuI}$ ,  $\text{BiOI}$ ,  $\text{SbOI}$ , which are insoluble;  $\text{PbI}_2$ ,  $\text{BiI}_3$  and  $\text{SnI}_2$  are slightly soluble.

*Carbonates* are generally insoluble; those of Na, K and  $\text{NH}_4$  are soluble. The *bicarbonates* of the alkali metals and of Ca, Sr, Ba, Mg, Fe and Mn are also soluble; those, other than the alkali metals, exist only in solution.

*Sulphides* are generally insoluble; those of Ba, Sr and Ca are slightly soluble; those of Na, K and  $\text{NH}_4$  are readily soluble.

*Sulphites* are generally insoluble; exceptions are those of the alkali metals, and the bisulphites of the alkaline earth group.

*Sulphates* are generally soluble; those of Pb, Hg (ous), Sr and Ba are insoluble; those of Ag, Hg (ic), Ca and a few basic sulphates (e.g. Bi and Hg) are slightly soluble.

*Phosphates, arsenates and arsenites* are generally insoluble; those of Na, K and  $\text{NH}_4$  are soluble.

*Fluorides* are generally insoluble; those of Na, K,  $\text{NH}_4$ , Ag and Hg (ous) are soluble.

*Borates*, with the exception of those of the alkali metals, are insoluble.

*Silicates* possess solubilities similar to those of the borates.

*Chromates* are generally insoluble or sparingly soluble; exceptions are those of the alkali metals and Ca, Sr, Mg, Mn, Zn, Fe and Cu.

*Thiocyanates* of Hg (ic), Cu (ic), Fe, Ca, Sr, Ba, Mg, Na, K and  $\text{NH}_4$  are soluble.

*Thiosulphates* are generally soluble; the Ag and Ba salts are sparingly soluble.

*Oxalates, formates, tartrates and citrates* are generally insoluble; those of Na, K and  $\text{NH}_4$  are soluble.

**Test (vi). Action of dilute sulphuric acid.**—Treat 0.1 gram of the substance in a small test-tube with 2 ml. of 2*N* sulphuric acid, and note whether any reaction takes place in the cold (indicated by *C*). Warm gently and observe the effect produced.

Observation	Inference
1. Colourless gas is evolved with effervescence; gas is odourless and produces turbidity when passed into lime water.* (C)	CO <sub>2</sub> from carbonate or bicarbonate.
2. Nitrous fumes evolved; recognised by reddish-brown colour, and turning starch-potassium iodide paper bluish-black. (C)	NO <sub>2</sub> from nitrite.
3. Yellowish-green gas evolved; suffocating odour, reddens and then bleaches litmus paper; turns starch-KI paper blue; <i>very poisonous</i> . (C)	Cl <sub>2</sub> from hypochlorite.
4. Odour of acetylene; burns with luminous, smoky flame. (C)	C <sub>2</sub> H <sub>2</sub> from carbide.
5. Colourless gas is evolved with suffocating odour; turns filter paper moistened with acidified potassium dichromate solution green; decolourises fuchsin solution.	SO <sub>2</sub> from sulphite.
6. Colourless gas is evolved; gives above tests for SO <sub>2</sub> ; sulphur is deposited in the solution.	SO <sub>2</sub> and S from thio-sulphate.
7. Colourless gas is evolved; odour of rotten eggs; blackens filter paper moistened with lead acetate solution; cadmium acetate paper turned yellow.	H <sub>2</sub> S from sulphide.†
8. Colourless gas is evolved; gives above tests for H <sub>2</sub> S; sulphur is deposited.	H <sub>2</sub> S and S from poly-sulphide.
9. Odour of vinegar.	H.C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> from acetate.
10. Colourless gas is evolved; odour of bitter almonds‡; <i>highly poisonous</i> .	HCN from cyanide or from soluble ferri- and ferro-cyanides.
11. Colourless gas is evolved; rekindles glowing splint.	O <sub>2</sub> from peroxides and per-salts of alkali and alkaline earth metals.
12. Colourless gas is evolved; pungent odour, reminiscent of SO <sub>2</sub> ; produces turbidity when passed into lime water.	CO <sub>2</sub> and a little HCNO from cyanate.
13. Upon boiling, yellow solution formed and SO <sub>2</sub> (fuchsin solution decolourised, etc.) evolved.	SO <sub>2</sub> , etc., from thio-cyanate.

**Test (vii). Action of concentrated sulphuric acid.**—Treat a small quantity (say, 0.1 gram) of the substance with 1–2 ml. of concentrated sulphuric acid, and warm the mixture gently; incline the mouth of the test-tube away from the

\* Magnesite, dolomite and a few other native carbonates give little or no CO<sub>2</sub> in the cold; CO<sub>2</sub> is readily evolved upon warming.

† Many sulphides, especially native ones, are not affected by dilute H<sub>2</sub>SO<sub>4</sub>; some H<sub>2</sub>S is evolved upon warming with concentrated HCl alone or with a little tin.

‡ If cyanide is suspected, gently warm (water bath) 5 mg. of the mixture in a small test-tube (e.g. 75 × 10 mm.) with 5–10 drops of 2N H<sub>2</sub>SO<sub>4</sub>; place a filter paper moistened at the centre with 1 drop of NaOH solution over the mouth of the tube. After 2 minutes, treat the drop on the paper with 1 drop of FeSO<sub>4</sub> solution, warm and add a drop or two of 6N HCl. A blue colour indicates the presence of a cyanide. For another test, see Section IV, 8, reaction 1. Mercuric cyanide is attacked slowly.

observer. (If chlorates or permanganates are suspected from the preliminary charcoal reduction tests to be present, very small quantities must be used (about 0.02 gram) as a dangerous explosion may occur on warming.)

If the substance reacted with dilute sulphuric acid, the addition of the concentrated acid may result in vigorous reaction and rapid evolution of gas, which may be accompanied by a very fine spray of the acid. In such a case, it is best to add dilute sulphuric acid dropwise to another portion of the substance until action ceases, and then to add 2-3 ml. of concentrated sulphuric acid.

The following results may be obtained.

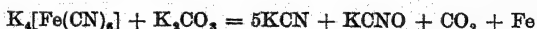
Observation	Inference
1. Colourless gas evolved with pungent odour and which fumes in the air; white fumes of $\text{NH}_4\text{Cl}$ in contact with glass rod moistened with concentrated $\text{NH}_3$ solution; $\text{Cl}_2$ evolved on addition of precipitated $\text{MnO}_2$ (bleaches litmus paper; turns KI-starch paper blue).	$\text{HCl}$ from <i>chloride</i> .
2. Gas evolved with pungent odour, reddish colour, and fumes in moist air; on addition of precipitated $\text{MnO}_2$ , increased amount of red fumes with odour of bromine (fumes colour moist starch paper orange-red or fluorescein paper red).	$\text{HBr}$ and $\text{Br}_2$ from <i>bromide</i> .
3. Violet vapours evolved, accompanied by pungent acid fumes, and often $\text{SO}_2$ and even $\text{H}_2\text{S}$ .	$\text{HI}$ and $\text{I}_2$ from <i>iodide</i> .
4. Reddish-brown fumes evolved (similar in colour to bromine); on passing into water, obtain chromic and hydrochloric acids, both readily identified (yellow ppt. of $\text{PbCrO}_4$ with excess of $\text{NH}_3$ solution, lead acetate solution and acetic acid; or by "perchromic acid" test).	$\text{CrO}_2\text{Cl}_2$ from <i>chloride in presence of chromate</i> .
5. Pungent acid fumes evolved, often coloured brown by $\text{NO}_2$ ; colour deepens upon addition of copper turnings (if nitrites absent).	$\text{HNO}_3$ and $\text{NO}_2$ from <i>nitrate</i> .
6. Yellow gas evolved in the cold with characteristic odour; explosion or crackling noise on warming ( <b>DANGER</b> ).	$\text{ClO}_2$ from <i>chlorate</i> .
7. Yellowish-green gas evolved; irritating odour; bleaches litmus paper; turns KI-starch paper blue; <i>very poisonous</i> .	$\text{Cl}_2$ from <i>chloride in presence of oxidising agents</i> .
8. "Oily" appearance of tube in cold; on warming, pungent gas evolved which corrodes the glass; if moistened glass rod introduced into the vapour, gelatinous ppt. of silicic acid is deposited upon it.	$\text{HF}$ from <i>fluoride or silicofluoride</i> .

[Continued overleaf

Observation	Inference
9. Purple fumes evolved with explosion (GREAT DANGER).	$Mn_2O_7$ from <i>perman-ganate</i> .
10. Colourless gas evolved; burns with blue flame; no charring.	CO from <i>formate, oxalate, cyanide, ferri-cyanide or ferro-cyanide</i> .*
11. Colourless gas evolved; renders lime water turbid and also burns with a blue flame; no blackening.	CO and $CO_2$ from <i>oxalate</i> .
12. Colourless gas evolved; burns with a blue flame and/or renders lime water turbid; as heating is continued, $SO_2$ is evolved and residue in tube (a) chars rapidly (odour of burnt sugar), (b) chars slowly, accompanied by irritant vapours.	$CO, CO_2$ and $SO_2$ from (a) <i>tartrate</i> , (b) <i>citrate</i> .
13. Irritating fumes evolved.	<i>Benzoate</i> .
14. Pungent odour of vinegar.	$H_2C_2H_3O_2$ from <i>acetate</i> .
15. Dark-crimson coloration of acid.	<i>Gallate</i> .
16. Brownish-purple coloration of acid.	<i>Tannate</i> .
17. Colourless gas evolved; rekindles glowing splint.	$O_2$ from <i>peroxides</i> , some <i>per-salts</i> or <i>chromate</i> .
18. Colourless gas evolved, burns with blue flame, deep blue solution produced.	CO and anhydrous $CoSO_4$ from <i>cobalti-cyanide</i> .†
19. Yellow coloration in cold; upon warming, vigorous reaction, COS (burns with blue flame), $SO_2$ (decolourises fuchsin solution, etc.) and free S produced.	$COS, SO_2$ and S from <i>thiocyanate</i> .
20. Red fumes of $Br_2$ (turn fluorescein paper red) and also $O_2$ evolved.	$Br_2$ and $O_2$ from <i>bromate</i> .

\* If ferro- and/or ferri-cyanides are present, they must be destroyed before proceeding with the analysis for cations because they would yield precipitates when the solution is acidified and boiled, and would also introduce other disturbing effects. This may be effected by heating about 1 gram of the mixture with 3-4 ml. of concentrated sulphuric acid in a porcelain crucible placed in an inclined position over the flame and directing the flame against the upper part of the crucible. The heating is continued until fumes of sulphur trioxide cease to be evolved. The residue is then treated with a little concentrated sulphuric acid, warmed gently and water added portionwise. The whole is then boiled for about 5 minutes, and filtered when cold. The filtrate may be analysed for all metals except lead, strontium and barium which, if present, will be found in the residue.

Alternatively, the complex cyanides may be eliminated from the mixture by fusing with an equal weight of sodium or potassium carbonate in a porcelain crucible. Soluble cyanates and cyanides are formed, which may be extracted with water; the residual metallic iron may be dissolved in dilute hydrochloric acid.



† Rarely encountered in routine qualitative analysis; a characteristic test is the white precipitate, insoluble in nitric acid, produced with ferrous sulphate solution (see under Cobalt, Section III, 24, reaction 4).

**Test (viii). Test for nitrate (or nitrite).**—If ammonium has been found {test (v)}, boiling is continued until ammonia can no longer be detected by its action upon mercurous nitrate paper or upon red litmus paper. Add a little (say, 0.1 gram) aluminium powder or zinc dust or finely powdered Devarda's alloy to the cooled solution and warm the mixture gently. Remove the flame as soon as evolution of hydrogen commences (with aluminium powder the reaction may become vigorous; cooling with tap water may be necessary to moderate the vigour of the reaction).

If ammonia is evolved, as detected by its odour, its action upon litmus paper and upon filter paper soaked in mercurous nitrate solution,\* then the presence of a nitrate or nitrite is indicated (compare Section IV, 18, reaction 4). The presence of a nitrite will generally also be detected in the reaction with dilute sulphuric acid {see test (vi)}; if nitrite be absent, then the presence of nitrate alone is indicated.

*Cyanides, thiocyanates, ferro- and ferri-cyanides also yield ammonia under these experimental conditions.* The reaction is somewhat slower for these anions; up to 5 minutes may elapse before ammonia can be detected from ferro- and ferri-cyanides. If these are present, or are suspected as a result of the preliminary tests, particularly that with concentrated sulphuric acid, they must first be removed as follows. Treat the " $\text{Na}_2\text{CO}_3$  prepared solution" with excess of nitrate-free silver sulphate, warm the mixture to about  $60^\circ$ , shake vigorously for 3–4 minutes, and filter from the silver salts of the interfering anions and excess of precipitant. Remove the excess of silver ions from the filtrate by adding an excess of sodium hydroxide solution and filter off the precipitated silver oxide. Evaporate the filtrate to about half bulk and test with zinc, aluminium or Devarda's alloy. If cyanides alone are present, they may be rendered innocuous by the addition of a little mercuric chloride solution.

**Test (ix). Borate test.**—Make a paste of the original substance with calcium fluoride and concentrated sulphuric acid. Hold some of this in a platinum loop just outside the base of the Bunsen flame. A green flame, due to boron trifluoride, indicates borates. Barium and copper do not interfere when the test is carried out in the above manner.

\* It must be emphasised that the mercurous nitrate paper test for ammonia is not applicable in the presence of arsenite. Arsenite is reduced by alkaline reducing agents to arsine, which blackens mercurous nitrate paper. The tannic acid–silver nitrate test (Section III, 36, reaction 7) may also be used: this test is likewise not applicable in the presence of arsenite.

Alternatively, the following test (which is strongly recommended) may be employed. Fit up the apparatus shown in Fig. VII, 3, 1, using rubber stoppers; the end of the right-angled bend should be drawn out into a capillary of not more than 0.5 mm. bore and 3-4 cm. long. The empty test-tube

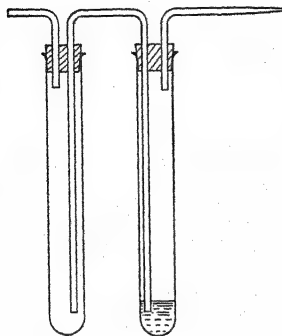


Fig. VII, 3, 1

acts as a trap between the mouth and the test-tube containing the solution under test to prevent the solution from reaching the mouth should the capillary become blocked.

Place about 0.1 gram of the substance in the test-tube, add 1-2 ml. of concentrated sulphuric acid with the aid of a dropper or small pipette, followed by 5-6 ml. of methyl alcohol in 1 ml. portions (caution!). Introduce the modified "wash-bottle" tubes and connect by a short length of rubber tubing to the trap. Blow gently through the liquid and direct

the vapours issuing from the capillary into a colourless Bunsen flame. If a borate is present, the flame will acquire a characteristic green colour due to the volatile methyl borate  $B(OCH_3)_3$ . Under these experimental conditions copper and barium, which colour the flame green, do not interfere.\*

## EXAMINATION FOR METAL IONS (CATIONS) IN SOLUTION

### VII, 4. PREPARATION OF A SOLUTION OF THE SOLID

Use small quantities (5-10 mg.) of the powdered solid and examine the solubility in the following solvents in the order given: (1) water, (2) dilute hydrochloric acid, (3) concentrated hydrochloric acid, (4) dilute nitric acid, (5) concentrated nitric acid and (6) aqua regia. Try the solubility first in the cold and then on warming; if in doubt whether the substance or a portion of the substance has dissolved, evaporate a little of the clear solution on a watch glass. If the substance dissolves in water, proceed immediately to test for the metal ions. If the

\* This procedure is simpler than that of Section IV, 45, 15; the latter, however, is fool-proof and perfectly unambiguous.



use of dilute hydrochloric acid results in the formation of a precipitate, this may consist of the metals of Group I; the precipitate may either be filtered off and examined for this group, or else the original substance may be dissolved in dilute nitric acid. If concentrated hydrochloric acid is employed for solution, it will be necessary to evaporate off most of the acid since certain metals of Group II (e.g. cadmium and lead) are not completely precipitated in the presence of large concentrations of acid. Where nitric acid has been used for the process of solution, all of the acid must be removed by evaporating nearly to dryness, adding a little hydrochloric acid, evaporating again to a small bulk and then diluting with water; these remarks also apply to aqua regia. For this reason nitric acid is often omitted from the solvents, and the tests confined to solvents 1, 2, 3 and 6.

When a suitable solvent has been found, the solution for analysis is prepared with 0.5–1 gram of the solid; the volume of the final solution should be 15–20 ml.

If the substance is insoluble in aqua regia (and in concentrated acids), it is regarded as *insoluble* and is treated by the special methods detailed in Section VII, 21 below.

## VII, 5. GENERAL SCHEME FOR THE SEPARATION OF THE CATIONS INTO GROUPS

Before describing the general scheme (for a simplified general scheme, see Section V, 8) for the separation of the metal ions into groups, the following facts are brought to the notice of the student as it is believed that by their proper understanding and appreciation, many of the usual pitfalls will be avoided.

(1) The analysis should not be conducted with large quantities of the substance because much time will be spent in filtering the precipitates and difficulty will be experienced in washing and dissolving them. It is therefore recommended that 0.5–1 gram should be employed for the analysis. After a little experience the student will be able to judge from the relative sizes of the precipitates, the relative quantities of the various components present in the mixture.

(2) The tests must, in the first place, be carried out in the order given. A group reagent will separate its particular group only from those which follow it and not from those which precede it. Thus hydrogen sulphide in the presence of 0.3N hydrochloric acid will separate Group II from Groups IIIA, IIIB, IV and V, but does not separate Group II from Group I.

It is most important therefore that one group should be completely precipitated before precipitation of the next group is attempted, otherwise the group precipitates will be contaminated by metals from the preceding groups, and misleading results will be obtained.

(3) The conditions for precipitation and for solution must be rigidly followed.

(4) All precipitates must be washed to remove adhering solution in order to avoid contamination by the metals remaining in the filtrate. The first washings should be added to the solution from which the precipitate has been filtered; later washings may be discarded.

(5) If the volume of the solution at any stage of the analysis becomes too large, it should be reduced by evaporation.

(6) All the apparatus employed in the analysis must be scrupulously clean. The use of dirty apparatus may be sufficient to introduce impurities into the substance under examination.

#### NOTES ON TABLE I (GENERAL TABLE FOR SEPARATION OF CATIONS INTO GROUPS)

(1) If the original substance was completely soluble in dilute HCl, it is evident that no silver or mercurous salt is present. When lead is present, the solution may be clear whilst hot, but  $\text{PbCl}_2$  is deposited on cooling the solution. Any lead missed in this group will be precipitated with  $\text{H}_2\text{S}$  in Group II.

A precipitate may form upon the addition of HCl to certain neutral or slightly acid solutions even when none of the Group I metals are present. This may occur under the following conditions:

(a) Aqueous solutions of Sb, Bi and Sn, not containing free HCl, precipitate as the oxychlorides upon the addition of this acid. The precipitate dissolves, however, upon the addition of excess of acid.

(b) Concentrated solutions of certain chlorides, *e.g.* NaCl and  $\text{BaCl}_2$ , may form precipitates upon the addition of HCl; these dissolve on diluting with water.

(c) Borates may yield a white crystalline precipitate of boric acid, particularly if the acid is concentrated; only partial precipitation may occur here.

(d) Silicates may yield a gelatinous precipitate of silicic acid; only partial precipitation may occur here.

(e) The thio-salts of arsenic, antimony and tin will give the corresponding sulphides.

(2) The  $\text{H}_2\text{O}_2$  solution is added to oxidise  $\text{Sn}^{++}$  to  $\text{Sn}^{++++}$ , thus leading ultimately to the precipitation of  $\text{SnS}_2$  in place of the somewhat gelatinous  $\text{SnS}$ . The excess of  $\text{H}_2\text{O}_2$  should preferably be decomposed by boiling before passing  $\text{H}_2\text{S}$ , otherwise some S may be precipitated. The subsequent separation of Groups IIA and IIB by

## I, 6.

**Table I.—Separation of Cations into Groups**  
(Organic Acids, Boric, Boric, Hydrofluoric, Silicic and Phosphoric Acids being present)

Add a few drops of dilute HCl to the cold solution. If a ppt. forms, continue adding dilute HCl until no further precipitation takes place. Filter.	
<b>Residue.</b> White. <b>Group I</b> <b>present.</b> Examine by Group separation table III (Section I, 8).	<b>Filtrate.</b> Add 1 ml. of 3% $H_2O_2$ solution (2). Adjust the HCl concentration to 0.3N (3). Heat nearly to boiling, and saturate with $H_2S$ under "pressure" (4). Filter.
<b>Residue.</b> Coloured. <b>Group II</b> <b>present.</b> Examine by Group separation tables IV or IVA (Section VII, 9), V (Section VII, 10) and VI or VIA (Section VII, 11).	<b>Filtrate.</b> Boil down in a porcelain dish to about 10 ml. and thus ensure that all $H_2S$ has been removed (test cautiously to dryness; moisten with 2-3 ml. of concentrated $HNO_3$ and heat gently; this will remove organic acids. If borate and fluoride are present (6), evaporate the residue repeatedly with 5-10 ml. of concentrated HCl. HCl and evaporate on a water bath (7). Add about 16 ml. of dilute HCl, warm and filter from any residue, originating from any silicate present (8). Test 0.5 ml. of the filtrate (or solution, if silicate is absent) for phosphate with 3 ml. of ammonium molybdate reagent and a few drops of concentrated $HNO_3$ , and warm to about 40°C: a yellow ppt. indicates phosphate is present. If phosphate is present (9), remove all phosphate ions by treatment with zirconium nitrate as detailed in Table II (Section VII, 7). If phosphate is absent, add 1-2 grams of solid $NH_4Cl$ , heat to boiling, add dilute $NH_3$ solution until mixture is alkaline and then 1 ml. in excess, boil for 1 minute and filter immediately.
<b>Residue.</b> <b>Group IIIA</b> <b>present.</b> Examine by Group separation Table VII (Section VII, 12). [Some $CaF_2$ may also precipitate here.]	<b>Filtrate.</b> Add 2-3 ml. of dilute aqueous $NH_3$ , heat, pass $H_2S$ (under "pressure") for 0.5-1 minute (10), filter and wash (11).
<b>Residue.</b> <b>Group IIIB</b> <b>present.</b> Examine by Group separation Table VIII (Section VII, 13).	<b>Filtrate</b> (12). Transfer to a porcelain dish and acidify with dilute acetic acid (13). Evaporate to a pasty mass [FUME CUPBOARD], allow to cool, add 3-4 ml. of concentrated $HNO_3$ so as to wash the solid round the walls to the centre of the dish, and heat cautiously until the mixture is dry. Then heat more strongly until all ammonium salts are volatilised (14). Cool. Add 3 ml. of dilute HCl and 10 ml. of water: warm and stir to dissolve the salts. Filter, if necessary. Add 0.25 gram of solid $NH_4Cl$ (or 2.5 ml. of 10% $NH_4Cl$ solution), render alkaline with concentrated $NH_3$ solution and then add, with stirring, $(NH_4)_2CO_3$ solution in slight excess. Keep and stir the solution in a water bath at 50-60°C for 3-5 minutes (15). Filter and wash with a little hot water.
<b>Residue.</b> White. <b>Group IV</b> <b>present.</b> Examine by Group separation Table IX or IXA (Section VII, 14).	<b>Filtrate</b> (16). Evaporate to a pasty mass in a porcelain dish [FUME CUPBOARD], add 3 ml. of concentrated $HNO_3$ so as to wash solid from walls to centre of dish, evaporate cautiously to dryness and then heat until white fumes of ammonium salts cease to be evolved. White residue. <b>Group V present.</b>
Examine by Group Separation Table X (Section VII, 15).	

means of aqueous KOH is thus rendered more complete since  $\text{SnS}_2$  dissolves entirely and  $\text{SnS}$  dissolves only partially in  $2N$  KOH.

If it is intended to use ammonium polysulphide in the separation of Groups IIA and IIB, the addition of  $\text{H}_2\text{O}_2$  is not essential since  $(\text{NH}_4)_2\text{S}_x$  will oxidise  $\text{SnS}$  to  $\text{SnS}_2$  and the latter dissolves as the thiostannate  $(\text{NH}_4)_2\text{SnS}_3$ .

(3) It is important that the concentration of HCl be approximately correct, *i.e.*  $0.3N$ , before passing  $\text{H}_2\text{S}$ : with higher concentrations of acid, lead, cadmium and stannous tin will be incompletely precipitated; if the acidity is too low, sulphides of Group IIB ( $\text{NiS}$ ,  $\text{CoS}$  and  $\text{ZnS}$ ) may be precipitated.

Either of two methods may be employed to adjust the acid concentration.

(a) Concentrate the solution until it has a volume of 10–15 ml. Cool. Add concentrated  $\text{NH}_3$  solution dropwise from a dropper pipette, with constant stirring, until the mixture is alkaline. (Ignore any precipitate which may form: this either dissolves when the HCl is added or else is converted into the sulphide by the  $\text{H}_2\text{S}$  treatment.) Introduce dilute HCl dropwise until the mixture is just acid (use litmus paper). Then add 2.0 ml. of  $3N$  HCl (measured from a graduated pipette or a calibrated dropper) and dilute the solution to a volume of 20 ml. with distilled water.

(b) An alternative procedure is to make use of the indicator methyl violet (0.1 per cent aqueous solution or, better, the purchased or prepared indicator paper). The following table gives the colour of the indicator at various concentrations of acid.

<i>Acid concentration</i>	<i>pH</i>	<i>Methyl violet indicator</i>
Neutral or alkaline	7+	Violet.
0.1N HCl	1.0	Blue.
0.25N HCl	0.6	Blue-green.
0.33N HCl	0.5	Yellow-green.
0.50N HCl	0.3	Yellow.

Add 1 drop of the methyl violet indicator solution and introduce dilute HCl or dilute aqueous  $\text{NH}_3$  (as necessary) dropwise and with constant stirring until the colour of the solution is yellow-green: a blue-green colour is almost but not quite acid enough, yet is acceptable for most analyses. (If the indicator paper is available, the thoroughly stirred solution should be spotted on fresh portions of the paper.) It is recommended that a comparison solution containing, say, 10 ml. of  $0.3N$  HCl and 1 drop of indicator be freshly prepared: this will facilitate the correct adjustment of the acidity. A more satisfactory standard is a buffer solution prepared by mixing 5 ml. of  $N$  sodium acetate and 10 ml. of  $N$  HCl: this solution has a pH of 0.5.

(4) For the passage of  $\text{H}_2\text{S}$  into the solution, the latter is placed in a small conical flask (one of 50 ml. capacity is suitable) and the "pressure" method used as detailed in Section II, 2, 7.

Heat the solution almost to boiling and pass in  $\text{H}_2\text{S}$ , whilst slowly shaking the flask with a swirling motion, until precipitation is complete: the latter will be apparent when bubbling either stops altogether or is reduced to a very slow rate of 1-2 bubbles per minute. Saturation is normally reached in 2-5 minutes. The best method of determining whether precipitation is complete is to filter off a portion of the solution and to test the filtrate with  $\text{H}_2\text{S}$ . If only a white precipitate or suspension of sulphur is obtained, the presence of an oxidising agent is indicated.

If an oxidising agent is present (e.g. a permanganate, dichromate or ferric salt), as is shown by the gradual separation of a fine white precipitate of sulphur and/or change in colour of the solution, it is usual to pass  $\text{SO}_2$  into the hot solution until reduction is complete, then to boil off the excess of  $\text{SO}_2$  (test with  $\text{K}_2\text{Cr}_2\text{O}_7$  paper) and finally to pass  $\text{H}_2\text{S}$ . Arsenates, in particular, are slowly precipitated by  $\text{H}_2\text{S}$ : they are therefore generally reduced by  $\text{SO}_2$  to arsenites and then precipitated as  $\text{As}_2\text{S}_3$  with  $\text{H}_2\text{S}$ , after prior removal of the excess of  $\text{SO}_2$  in order to avoid interaction of the latter with  $\text{H}_2\text{S}$  and the consequent separation of S. Stannic compounds may be very slightly reduced to the stannous state by this treatment; the amount of reduction is, however, so small that it may be neglected. The original solution or substance must be tested for the valence state of the arsenic.

The objection to the use of  $\text{SO}_2$  is that some sulphuric acid may be formed, especially upon boiling, and this may partially precipitate Pb, Sr and Ba as sulphates. Any precipitate formed in this process should accordingly be examined for these cations:  $\text{PbSO}_4$  is soluble in ammonium acetate solution.

An alternative procedure to be borne in mind when arsenate, etc., is present, which does not possess the disadvantages associated with  $\text{SO}_2$  and is perhaps more expeditious, is to add 2-3 ml. of concentrated HCl and 0.5 ml. of 10 per cent ammonium iodide solution. The arsenate is thereby reduced to arsenite, and upon saturation of the hot solution with  $\text{H}_2\text{S}$  under "pressure," the arsenic is completely precipitated as  $\text{As}_2\text{S}_3$ . This reduction can be carried out after the sulphides of the other elements have been precipitated in the presence of 0.3N HCl.

The precipitated sulphides may be washed with a wash liquid prepared by dissolving 0.25 gram of  $\text{NH}_4\text{NO}_3$  in 5 ml. of water and treating this solution with  $\text{H}_2\text{S}$ . The  $\text{H}_2\text{S}$  must be present in the wash liquid to prevent oxidation of some of the moist sulphides to sulphates.

(5) Nitric acid is added to oxidise ferrous iron to the ferric state; if ferric iron was originally present, it will have been reduced by the  $\text{H}_2\text{S}$ . Alternatively, bromine water may be used for the oxidation: the excess of bromine must be removed by boiling. Ferrous iron is incompletely precipitated by  $\text{NH}_3$  solution in the presence of  $\text{NH}_4\text{Cl}$ .

Organic acids interfere with the normal course of analysis. Thus in the presence of oxalic, tartaric or citric acids, the addition of the group reagent  $\text{NH}_4\text{Cl}$  and  $\text{NH}_3$  solution might fail to cause the precipitation of the hydroxides of Fe, Al and Cr. Furthermore, if oxalic acid is present, the oxalates of some of the metals of Groups IIIB, IV and of Mg, which are insoluble in ammoniacal solution, might be precipitated at this stage. It is therefore essential to destroy the organic acids, the presence of which has been indicated in the preliminary tests, before precipitation of Group IIIA. This is best effected by evaporation with concentrated nitric acid until the black residue is completely oxidised. It is important not to heat the residue too strongly as it may convert any Fe, Al or Cr present into the form of the sesquioxide which is difficultly soluble in concentrated HCl.

If benzoic and/or salicylic acid are present, the free acids will separate upon the addition of HCl and they should therefore be looked for in the Group I precipitate. If any salicylic acid should pass through to Group III, great care must be taken when evaporating to dryness with concentrated  $\text{HNO}_3$  since the nitro-salicylic acids explode on strong heating.

(6) Borates and fluorides of the metals of Group IIIB, IV and of Mg are insoluble (or sparingly soluble) in ammoniacal solution, and are therefore liable to be precipitated at this stage. They may be removed by repeated evaporation with concentrated HCl; the boric acid will slowly volatilise in the steam and the hydrogen fluoride with the excess of HCl.

(7) Boric acid alone is more rapidly eliminated as the volatile methyl borate  $\text{B}(\text{OCH}_3)_3$  (*highly poisonous*). If much boric acid is present, two treatments with  $\text{CH}_3\text{OH}$  and HCl may be required.

(8) Unless silicates are removed here, they are likely to be confused with  $\text{Al}(\text{OH})_3$  in the group separation. Repeated evaporation with concentrated HCl converts silicates into a granular form of hydrated silica, which is readily filtered, particularly after a final digestion with dilute HCl. The precipitate should be subjected to the microcosmic salt bead test or to the silicon tetrafluoride test (Section IV, 26).

Solutions of silicates are decomposed by dilute HCl into silicic acid, which may partially separate in Group I in the gelatinous form. That not precipitated in Group I will be precipitated by  $\text{NH}_4\text{Cl}$  solution in Group IIIA (see under Silicates, Section IV, 26, reaction 2).

(9) The phosphates of the metals of Group IIIA, IIIB, IV and of Mg are insoluble in water and in ammoniacal solution, and may be precipitated at this stage. An excellent method for the removal of phosphate is given in Table II (Section VII, 7).

(10) It is recommended that a small portion of the filtrate from Group IIIA be tested first with a little aqueous  $\text{NH}_3$  and  $\text{H}_2\text{S}$ . If a precipitate is obtained, the main solution should be treated in this

manner. If there is no precipitate, metals of Group IIIB are absent and the main filtrate from Group IIIA may then be employed in testing for Group IV, etc.

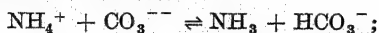
The student should remember that the conditions for the precipitation of Group IIIB differ from those in Group II. In the latter Group,  $\text{H}_2\text{S}$  is passed into an acid solution in which the gas is only slightly soluble and hence much of it escapes unabsorbed unless the "pressure" technique is employed. In the former Group, the solution is alkaline and therefore the  $\text{H}_2\text{S}$  is readily absorbed. Moreover, if too much  $\text{H}_2\text{S}$  is employed,  $\text{NiS}$  may partially form a colloidal solution. This is largely avoided by passing  $\text{H}_2\text{S}$  for 30–60 seconds, and testing for completeness of precipitation. Some authors recommend that  $\text{H}_2\text{S}$  be passed into a solution acidified with acetic acid and thus avoid the complication due to colloidal  $\text{NiS}$ .

(11) The wash liquid for the Group IIIB precipitate may consist of 1 per cent  $\text{NH}_4\text{Cl}$  to which 1 per cent by volume of ammonium sulphide solution is added. Oxidation of the moist sulphides to the soluble sulphates is thus considerably reduced.

(12) If the solution or the filtrate from Group IIIB is brown or dark in colour,  $\text{Ni}$  may be suspected. The dark-coloured solution contains colloidal  $\text{NiS}$ , which runs through the filter paper. It may be acidified with acetic acid, and then boiled until the  $\text{NiS}$  has coagulated: this may either be added to the Group IIIB precipitate or tested separately for  $\text{Ni}$ . As a general rule, the addition of macerated filter paper (e.g. in the form of a portion of a Whatman filtration accelerator or ashless tablet) to the suspension before filtration will lead to a clear or colourless solution.

(13) The filtrate must be acidified immediately and concentrated to remove  $\text{H}_2\text{S}$ . Ammonium sulphide solution on exposure to air slowly oxidises to ammonium sulphate and would then precipitate any barium or strontium present as  $\text{BaSO}_4$  or  $\text{SrSO}_4$ . Another reason for the immediate acidification of the filtrate from Group IIIB is to prevent the absorption of  $\text{CO}_2$  from the air with the attendant formation of carbonate ions: the latter would also precipitate the ions of Group IV.

(14) The initial filtrate from Group IIIB will contain a very high concentration of ammonium salts. The concentration of ammonium ions is much greater than is necessary to prevent the precipitation of  $\text{Mg}(\text{OH})_2$  and it may also lead to incomplete precipitation of the carbonates of Group IV metals. The latter effect is due to the acidic properties of the ammonium ion:



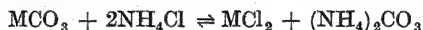
the concentration of  $\text{CO}_3^{--}$  ions upon the addition of  $(\text{NH}_4)_2\text{CO}_3$  would thus be reduced considerably. For these reasons most of the ammonium salts must be eliminated first.

Concentrated  $\text{HNO}_3$  decomposes  $\text{NH}_4\text{Cl}$  at a lower temperature than is required for its volatilisation:



Loss by decrepitation and spurting during this operation must be avoided.

(15) The "ammonium carbonate solution" contains much ammonium bicarbonate  $\text{NH}_4\text{HCO}_3$  and will accordingly form soluble bicarbonates with the alkaline earth metals unless excess of ammonia solution is present; in the latter case the amount of normal carbonate  $(\text{NH}_4)_2\text{CO}_3$  present will be increased. When precipitating Group IV, the solution should be warm (*ca.*  $50^\circ\text{C}$ ) to decompose any bicarbonates formed. The solution must not, however, be boiled because the reaction



is reversible; boiling decomposes the  $(\text{NH}_4)_2\text{CO}_3$ , the reaction will proceed from left to right and the precipitate will dissolve (see also Section III, 29, reaction 2).

Ammonium carbonate decomposes appreciably above  $60^\circ\text{C}$ :



The digestion also improves the filtering properties of the precipitate.

(16) Owing to the slight solubility of  $\text{CaCO}_3$ ,  $\text{SrCO}_3$  and  $\text{BaCO}_3$  in solutions of ammonium salts, the filtrate from Group IV will, when these metals are present, contain minute amounts of the ions of the alkaline earth metals. Since the Group IV metals may interfere to a limited extent with the flame tests for Na and K and also with the  $\text{Na}_2\text{HPO}_4$  test for Mg (if employed), it has been recommended that the filtrate from Group IV be heated with a little (say, 1 ml.) of  $(\text{NH}_4)_2\text{SO}_4$  solution and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution and filtered from any precipitate which forms. Owing to the comparatively small concentration of ammonium salts, this is generally unnecessary if the procedure described in Table X (Section VII, 15) is adopted.

#### NOTES ON PHOSPHATE SEPARATION TABLE (TABLE II)

(1) The HCl concentration should not exceed *N*, otherwise a turbid supernatant liquid is obtained and the precipitation of phosphate is not quantitative.

(2) This is usually termed the zirconium nitrate reagent. Its preparation is described in the Appendix (Section A, 2).

(3) It is important that the excess of the zirconium nitrate reagent should not exceed 25 per cent, otherwise a turbid supernatant liquid will be obtained: this turbidity cannot be removed by filtration or centrifugation. It is best, therefore, to add the zirconium nitrate solution slowly and with stirring until precipitation appears complete, heat just to boiling, filter and test the filtrate with the reagent, etc.

(4) The addition of half a Whatman filtration accelerator (or a little filter paper pulp) assists filtration; the precipitate must be washed thoroughly with hot water. The filtration accelerator consists of compressed filter paper which disintegrates on boiling; it



## VII, 7. Table II.—Phosphate Separation Table (Zirconyl Nitrate Method)\*

Reduce the volume of the solution to about 10 ml. by evaporation, if necessary. Adjust the HCl concentration so that it does not exceed *N* (1). Add 0.5–1 gram of solid  $\text{NH}_4\text{Cl}$ , stir until dissolved and then add zirconyl nitrate reagent (2) slowly and with stirring until precipitation is complete (3); a large excess of the reagent must be avoided. Heat the contents of the test-tube or small conical flask just to boiling and stir with a glass rod to prevent bumping. Filter through a Whatman No. 32 filter paper (4). Wash the ppt. with a little hot water, and combine the washings with the filtrate.

**Residue.**  
Zirconium  
phosphate.  
Reject.

**Filtrate.** Test if all phosphate has been precipitated by the addition of a drop of the zirconyl nitrate reagent. Add about 0.5 gram of solid  $\text{NH}_4\text{Cl}$ , heat to boiling, add a slight excess of dilute  $\text{NH}_3$  solution (*i.e.* until the odour of  $\text{NH}_3$  is permanent in the boiling solution), boil for 2–3 minutes and filter.

**Residue.** Examine for Group IIIA by Group Separation Table IX or IXA (Section VII, 14). The excess of Zr will be found in the residue after treatment with  $\text{H}_2\text{O}_2$  and NaOH solution (or with sodium perborate  $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$  and boiling), and will accompany any  $\text{Fe}(\text{OH})_3$  if Fe is present.

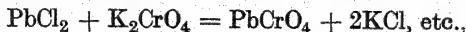
**Filtrate.** Examine for Groups IIIB, IV and V as detailed in General Table I (Section VII, 6).

increases the speed of filtration by retaining part of the precipitate and thus preventing the clogging of the pores of the filter paper.

### Explanation (Table III)

The metal ions of lead, silver and mercurous mercury are precipitated by dilute HCl as the insoluble chlorides  $\text{PbCl}_2$ ,  $\text{AgCl}$  and  $\text{Hg}_2\text{Cl}_2$  respectively; the chlorides of all the other common metals are soluble. The separation of these is based upon the following facts:

(1)  $\text{PbCl}_2$  is soluble in boiling water, whilst  $\text{Hg}_2\text{Cl}_2$  and  $\text{AgCl}$  are insoluble. Extraction of the precipitate with hot water therefore removes the  $\text{PbCl}_2$ . Confirmatory tests for lead ions are applied to the solution so obtained, *e.g.*



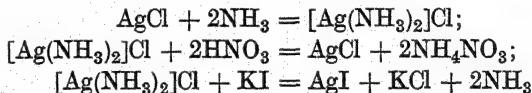
(for details, see under Lead, Section III, 2).

\* For an alternative, but less satisfactory, phosphate separation, see Table I (Section VIII, 2).

## VII, 8. Table III.—Analysis of Group I (Silver Group)

<p>The ppt. may contain <math>\text{PbCl}_2</math>, <math>\text{AgCl}</math> and <math>\text{Hg}_2\text{Cl}_2</math>. Wash the ppt. on the filter first with 2 ml. of 1-2N <math>\text{HCl}</math>, then 2-3 times with 1 ml. portions of cold water and reject the washings with water. Transfer the ppt. to a small beaker or to a boiling tube, and boil with 5-10 ml. of water. Filter hot.</p>		
<p><b>Residue.</b> May contain <math>\text{Hg}_2\text{Cl}_2</math> and <math>\text{AgCl}</math>. Wash the ppt. several times with hot water until the washings give no ppt. with <math>\text{K}_2\text{CrO}_4</math> solution: this ensures the complete removal of the Pb.</p> <p>Pour 3-4 ml. of warm dilute <math>\text{NH}_3</math> solution over the ppt. and collect the filtrate.</p>		<p><b>Filtrate.</b> May contain <math>\text{PbCl}_2</math>.</p> <p>Cool a portion of the solution: a white crystalline ppt. of <math>\text{PbCl}_2</math> is obtained if Pb is present in any quantity.</p> <p>Divide the filtrate into 3 parts:</p> <p>(i) Add <math>\text{K}_2\text{CrO}_4</math> solution. Yellow ppt. of <math>\text{PbCrO}_4</math>, insoluble in dilute acetic acid.</p> <p>(ii) Add <math>\text{KI}</math> solution. Yellow ppt. of <math>\text{PbI}_2</math>, soluble in boiling water to a colourless solution, which deposits brilliant yellow crystals upon cooling.</p> <p>(iii) Add dilute <math>\text{H}_2\text{SO}_4</math>. White ppt. of <math>\text{PbSO}_4</math>, soluble in ammonium acetate solution.</p>
<p><b>Residue.</b> If black, consists of <math>\text{Hg}(\text{NH}_2)\text{Cl} + \text{Hg}</math>.</p> <p><b>Hg (ous) present.*</b></p>	<p><b>Filtrate.†</b> May contain <math>[\text{Ag}(\text{NH}_3)_2]\text{Cl}</math>. Divide into 3 parts:</p> <p>(i) Acidify with dilute <math>\text{HNO}_3</math>. White ppt. of <math>\text{AgCl}</math>.</p> <p>(ii) Add a few drops of <math>\text{KI}</math> solution. Pale yellow ppt. of <math>\text{AgI}</math>.</p> <p>(iii) Add a few drops of the rhodanine reagent.</p> <p><b>Ag present.</b></p>	<p><b>Pb present.</b></p>

(2)  $\text{AgCl}$  is soluble in dilute  $\text{NH}_3$  solution, yielding the soluble complex salt  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$ . The solution of this complex salt is decomposed by both dilute  $\text{HNO}_3$  and by  $\text{KI}$  solution with the precipitation of the insoluble salts  $\text{AgCl}$  and  $\text{AgI}$  respectively.



\* This is a conclusive test for mercurous mercury. It may be further confirmed by dissolving the ppt. in 3-4 ml. of boiling aqua regia, diluting, filtering if necessary, and then adding  $\text{SnCl}_2$  solution. A white ppt. ( $\text{Hg}_2\text{Cl}_2$ ), turning grey ( $\text{Hg}$ ), is obtained.

† If  $\text{Hg}$  is present in reasonably large quantity and  $\text{Ag}$  has not been detected, carry out the above confirmatory test for  $\text{Hg}$ , and treat the thoroughly washed residue, insoluble in aqua regia, with dilute  $\text{NH}_3$  solution. Filter, if necessary, and add dilute  $\text{HNO}_3$  to the clear solution. A white ppt. of  $\text{AgCl}$  will form if small amounts of  $\text{Ag}$  are present. This is an alternative procedure for separating  $\text{Hg}$  and  $\text{Ag}$  in  $\text{Hg}_2\text{Cl}_2$ - $\text{AgCl}$  mixture.

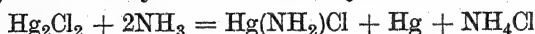
When the amount of  $\text{Hg}(\text{NH}_2)\text{Cl} + \text{Hg}$  is large and that of  $\text{AgCl}$  is small, the latter may be reduced to metallic silver according to the reaction,



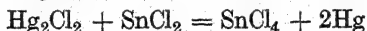
and thus escape detection.

The rhodanine reagent (Section III, 4, reaction 7) gives a precipitate with a solution of  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$ : any interference by mercury (or cuprous copper) is thus eliminated.

(3) The conversion of  $\text{Hg}_2\text{Cl}_2$  by dilute  $\text{NH}_4\text{OH}$  solution into the insoluble black mixture of amino mercuric chloride  $\text{Hg}(\text{NH}_2)\text{Cl}$  and finely divided mercury.



Aqua regia converts the black mixture into  $\text{HgCl}_2$  (see under Mercury (Section III, 3, reaction 1)). The mercuric ion is then detected with  $\text{SnCl}_2$  solution.



## VII, 9. Table IV.—Analysis of Group II (Copper and Arsenic Groups). Separation of Group IIA (Copper Group) and Group IIB (Arsenic Group)

### Method A

The ppt. may consist of the sulphides of the Group IIA metals ( $\text{HgS}$ ,  $\text{PbS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{CuS}$ ,  $\text{CdS}$ ) and those of Group IIB ( $\text{As}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{SnS}_2$ ,  $\text{SnS}$ ,  $\text{SnS}_4$ ). Wash the precipitated sulphides with a little 5%  $\text{NH}_4\text{Cl}$  solution that has been saturated with  $\text{H}_2\text{S}$  (the latter to prevent conversion of  $\text{CuS}$  into  $\text{CuSO}_4$  by atmospheric oxidation), transfer to a porcelain dish, add about 5 ml. of yellow ammonium sulphide solution, heat to  $50\text{--}60^\circ\text{C}$ ,\* and maintain at this temperature for 3–4 minutes with constant stirring. Filter.†

**Residue.** May contain  $\text{HgS}$ ,  $\text{PbS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{CuS}$  and  $\text{CdS}$ .

Wash once or twice with small volumes of dilute (1 : 100) ammonium sulphide solution, then with 1%  $\text{NH}_4\text{NO}_3$  solution and reject all washings.

**Group IIA present.**

**Filtrate.** May contain solutions of the thio-salts  $(\text{NH}_4)_3\text{AsS}_4$ ,  $(\text{NH}_4)_3\text{SbS}_4$  and  $(\text{NH}_4)_2\text{SnS}_3$ . Just acidify by adding concentrated  $\text{HCl}$  dropwise (test with litmus paper), and warm gently.

A yellow or orange ppt., which may contain  $\text{As}_2\text{S}_3$ ,  $\text{As}_2\text{S}_5$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_5$  and  $\text{SnS}_2$ ,‡ indicates Group IIB present.

### Explanation (Table IV)

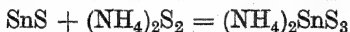
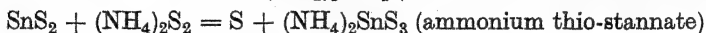
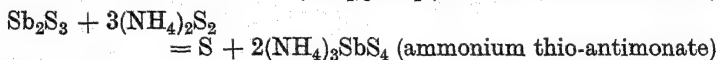
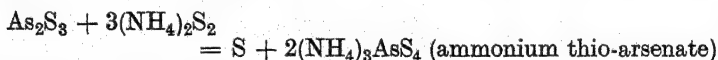
The sulphides of mercuric mercury, lead, bismuth, copper and cadmium and of arsenic, antimony and tin are precipitated by  $\text{H}_2\text{S}$  in the presence of dilute (0.3N)  $\text{HCl}$ . The sulphides

\* If the ammonium sulphide extract is boiled for some time in the air, a red antimony oxysulphide  $\text{Sb}_2\text{OS}_2$  may be precipitated.

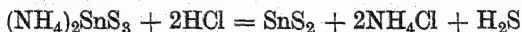
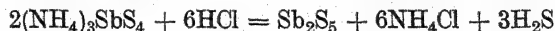
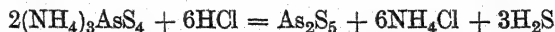
† If the precipitate is completely soluble in yellow ammonium sulphide solution, Group IIA is absent.

‡ If much S and little sulphide is suspected, shake with a little benzene: the sulphides collect at the boundary surface.

of arsenic ( $\text{As}_2\text{S}_3$ ), antimony ( $\text{Sb}_2\text{S}_3$  and  $\text{Sb}_2\text{S}_5$ ) and of tin ( $\text{SnS}_2$ ) (Group IIB) are soluble in yellow ammonium sulphide solution forming thio-salts, whilst those of the other metals (Group IIA) are insoluble. Stannous sulphide  $\text{SnS}$  is insoluble and antimony trisulphide  $\text{Sb}_2\text{S}_3$  is sparingly soluble in colourless ammonium sulphide solution, but both of these dissolve readily in the yellow ammonium sulphide solution; the  $\text{SnS}$  is converted into the thio-stannate. Colourless ammonium sulphide solution consists largely of ammonium hydrosulphide  $\text{NH}_4\text{HS}$  (the normal ammonium sulphide  $(\text{NH}_4)_2\text{S}$  does not seem to exist in aqueous solution). The yellow ammonium sulphide solution contains an excess of sulphur and may be formulated  $(\text{NH}_4)_2\text{S}_x$ : the formula  $(\text{NH}_4)_2\text{S}_2$  is often used for the last-named in writing equations, but there is some evidence that the solution contains the pentasulphide  $(\text{NH}_4)_2\text{S}_5$ . Yellow ammonium sulphide and not colourless ammonium sulphide is therefore generally used in one method for the separation of Groups IIA and IIB. The separation of sulphur upon acidification is a disadvantage.



Upon acidifying the solutions of the thio-salts with dilute  $\text{HCl}$ , the sulphides are precipitated, and the excess of ammonium sulphide is decomposed.



#### *Explanation (Table IVA)*

By digesting the Group II precipitate with 2*N*  $\text{KOH}$  solution, the sulphides of As, Sb and Sn (ic) dissolve whilst those of Hg, Pb, Bi, Cu and Cd are largely unattacked. The very slight solubility of  $\text{PbS}$  is reduced by adding a little  $\text{H}_2\text{S}$  water (i.e.  $\text{S}^{--}$ ): some  $\text{HgS}$  will dissolve in the presence of  $\text{S}^{--}$  and, in consequence, provision is made for the detection of Hg in both Groups IIA and IIB.

# VII, 9. Table IVA.—Analysis of Group II (Copper and Arsenic Groups). Separation of Group IIA (Copper Group) and Group IIB (Arsenic Group)

## Method B

The ppt. may consist of the sulphides of the Group IIA metals (HgS, PbS, Bi<sub>2</sub>S<sub>3</sub>, CuS and CdS) and those of Group IIB (As<sub>2</sub>S<sub>3</sub>, Sb<sub>2</sub>S<sub>3</sub>, Sb<sub>2</sub>S<sub>5</sub> and SnS<sub>2</sub>\*). Wash the precipitated sulphides with a small volume of 5% NH<sub>4</sub>Cl solution that has been saturated with H<sub>2</sub>S. Transfer the ppt. to a 100 ml. beaker or porcelain basin, add 10 ml. of 2N KOH solution and boil with constant stirring (CAUTION†) for 2–3 minutes. Add 3 ml. of freshly prepared, saturated H<sub>2</sub>S water, stir and filter (preferably through a double filter). Wash the residue with a little water and collect the washings with the filtrate.

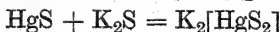
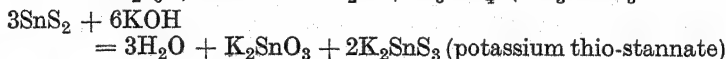
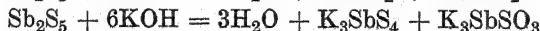
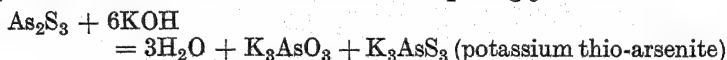
**Residue.** May contain HgS, PbS, Bi<sub>2</sub>S<sub>3</sub>, CuS and CdS.

**Group IIA present.**  
Reserve the ppt. for analysis by Table V.

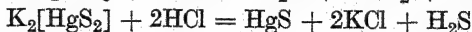
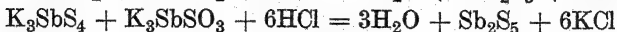
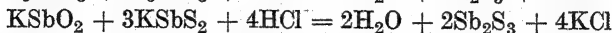
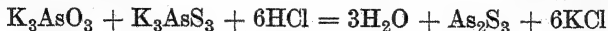
**Filtrate.** May contain KAsO<sub>3</sub>, KAsS<sub>3</sub>, K<sub>2</sub>Sn(OH)<sub>6</sub>, K<sub>2</sub>SnS<sub>3</sub> and a little K<sub>2</sub>[HgS<sub>2</sub>]. Transfer to a small conical flask or beaker, add concentrated HCl dropwise and with stirring until the mixture is distinctly acid to litmus paper. Treat with H<sub>2</sub>S for 2 minutes to ensure complete precipitation of the sulphides. The formation of a ppt. indicates the possible presence of Hg, As, Sb or Sn. Filter and wash the ppt. with a little water. Reserve the residue for analysis by Table VIA.

**Group IIB present.**

Potassium hydroxide is employed in preference to sodium hydroxide since sodium antimonate is sparingly soluble.



Upon acidification with HCl, the sulphides are precipitated:



\* Stannous sulphide is not completely soluble in 2N KOH. The oxidation with H<sub>2</sub>O<sub>2</sub> solution will have converted Sn<sup>++</sup> into Sn<sup>++++</sup> (see Table I).

† Potassium hydroxide is an extremely dangerous substance because of its destructive effect upon the eyes. Precipitates, when heated with KOH solution, tend to bump. Suitable precautions should therefore be taken: the process should be carried out in the fume cupboard.

The disadvantages attending the use of ammonium polysulphide in the separation of Groups IIA and IIB are:

- (i) Some CuS and HgS are dissolved.
- (ii) In the presence of large quantities of the Copper Group, small amounts of tin may escape detection.
- (iii) Acidification of the ammonium polysulphide extract leads to the precipitation of sulphur, which may obscure the presence of sulphides of Group IIB.
- (iv) Ammonium polysulphide solution, unless freshly prepared, may contain sulphate and this will lead to the precipitation of barium as BaSO<sub>4</sub>, etc.

*Explanation (Table V)*

The residue insoluble in yellow ammonium sulphide solution or in 2*N* KOH solution may contain HgS, PbS, Bi<sub>2</sub>S<sub>3</sub>, CuS and CdS. Their separation is based upon the following facts:

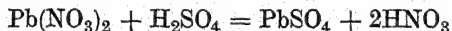
- (1) HgS is insoluble in dilute HNO<sub>3</sub>; the sulphides of Pb, Bi, Cu and Cd dissolve with the formation of nitrates.



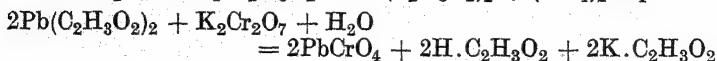
One confirmatory test for Hg involves the conversion of the HgS by aqua regia or by NaOCl-HCl into HgCl<sub>2</sub>, and the familiar reduction of the latter by SnCl<sub>2</sub> solution.\*



- (2) The filtrate from the nitric acid treatment contains the nitrates of Pb, Bi, Cu and Cd. Dilute H<sub>2</sub>SO<sub>4</sub> precipitates Pb as PbSO<sub>4</sub>, leaving the other metals (which form soluble sulphates) in solution.



The object of the evaporation with H<sub>2</sub>SO<sub>4</sub> until white fumes appear is to eliminate the HCl and HNO<sub>3</sub>, which have a slight solvent action upon the PbSO<sub>4</sub>. The PbSO<sub>4</sub> is converted by ammonium acetate solution into lead acetate, which is only feebly ionised in the presence of excess of acetate ions. The insoluble PbCrO<sub>4</sub> is precipitated upon the addition of K<sub>2</sub>CrO<sub>4</sub> or K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution.



\* Confirmatory tests will not, in general, be described in detail where they have already been given under the reactions of the metal ions.

## VII, 10. Table V.—Analysis of Group IIA (Copper Group)\*

The ppt. may contain  $\text{HgS}$ ,  $\text{PbS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{CuS}$  and  $\text{CdS}$ . Transfer to a beaker† or porcelain basin, add 5–10 ml. of dilute  $\text{HNO}_3$ , boil gently for 2–3 minutes, filter and wash with a little water.

**Residue.**

Black:  $\text{HgS}$ .

Dissolve in a mixture of 2.5 ml. of 10%  $\text{NaOCl}$  solution and 0.5 ml. of dilute  $\text{HCl}$ . Add 1 ml. of dilute  $\text{HCl}$ , boil off excess of  $\text{Cl}_2$  and cool. Add  $\text{SnCl}_2$  solution.

White ppt., turning grey or black.

**Hg (ic) present.**

**Filtrate.** May contain nitrates of Pb, Bi, Cu and Cd.

Test a small portion for Pb by adding dilute  $\text{H}_2\text{SO}_4$  and alcohol. A white ppt. of  $\text{PbSO}_4$  indicates **Pb present**. If Pb present, add dilute  $\text{H}_2\text{SO}_4$  to the remainder of the solution, concentrate in the fume cupboard until white fumes (from the dissociation of the  $\text{H}_2\text{SO}_4$ ) appear. Cool, add 10 ml. of water, stir, allow to stand 2–3 minutes, filter and wash with a little water.

**Residue.**

White:

$\text{PbSO}_4$ .

Pour 2 ml.

of ammon-

ium acetate

through

the filter

several

times, add

to the fil-

trate a few

drops of

dilute acetic

acid and

then  $\text{K}_2\text{CrO}_4$

solution.

Yellow ppt.

of  $\text{PbCrO}_4$ .

**Pb present.**

**Filtrate.** May contain nitrates and sulphates of Bi, Cu and Cd. Add concentrated  $\text{NH}_3$  solution until solution is distinctly alkaline. Filter.

**Residue.**

White: may be  $\text{Bi}(\text{OH})_3$ . Wash. Dissolve in the minimum volume of dilute  $\text{HCl}$  and pour into cold sodium stannite solution.†

Black ppt.

**Bi present.**

Alternatively, dissolve a little of ppt. in 2–3 drops of dilute  $\text{HNO}_3$ . Place 1 drop of this solution upon filter paper moistened with cinchonine-KI reagent.

Orange-red spot.

**Bi present.**

**Filtrate.** May contain

$[\text{Cu}(\text{NH}_3)_4]^{++}$  and

$[\text{Cd}(\text{NH}_3)_4]^{++}$ .

If deep blue in colour, Cu is present in quantity. Confirm Cu§ by acidifying a portion of the filtrate with dilute acetic acid and add  $\text{K}_4[\text{Fe}(\text{CN})_6]$  solution.

Reddish-brown ppt.

**Cu present.**

To the remainder of the filtrate, add  $\text{KCN}$  solution|| dropwise until colour is discharged, and add a further ml. in excess. Pass  $\text{H}_2\text{S}$  for 20–30 seconds.

Yellow ppt., sometimes discoloured, of  $\text{CdS}$ .

**Cd present.**

Filter off ppt. and dissolve a portion of it in 1 ml. of dilute  $\text{HCl}$ : boil to expel  $\text{H}_2\text{S}$  and most of the acid and apply the "cation-2B" test on 1 drop of the solution. A pink spot confirms Cd.¶

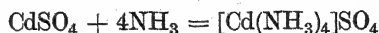
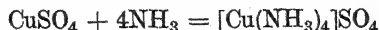
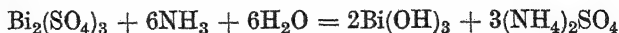
\* For an alternative Table, which is strongly recommended, see Section III, 10, Table IIA.

† This is most easily effected by making a small hole in the filter with a pointed glass rod, and washing the ppt. into the beaker or basin with dilute  $\text{HNO}_3$ .

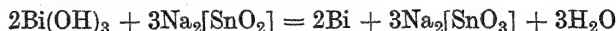
‡ Sodium stannite is prepared by adding  $\text{NaOH}$  solution to 1 ml. of  $\text{SnCl}_2$  solution until the ppt. of  $\text{Sn}(\text{OH})_2$  first formed redissolves.

§ Alternatively, just acidify a small portion with dilute  $\text{H}_2\text{SO}_4$ . Add 1 drop of this solution to a few drops of dilute  $\text{ZnSO}_4$  solution, and then introduce a little ammonium mercuri-thiocyanate reagent. A violet ppt. confirms Cu. The ppt. can be rendered clearly visible by adding a little amyl alcohol and shaking: it collects in and colours the organic layer.

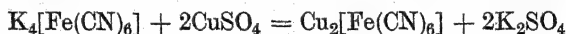
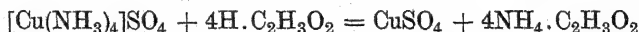
(3) The addition of *excess* of  $\text{NH}_3$  solution results in the precipitation of  $\text{Bi}(\text{OH})_3$  and the formation of the soluble complex salts,  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$  and  $[\text{Cd}(\text{NH}_3)_4]\text{SO}_4$ .



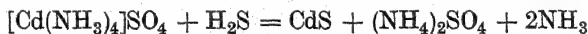
The sodium stannite solution reduces the  $\text{Bi}(\text{OH})_3$  to Bi and is itself oxidised to sodium stannate.



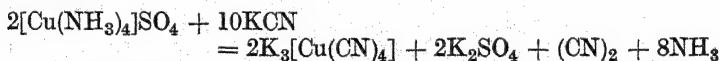
(4) The addition of acetic acid to the blue solution decomposes the complex into  $\text{CuSO}_4$  and  $\text{NH}_4 \cdot \text{C}_2\text{H}_3\text{O}_2$ ;  $\text{K}_4[\text{Fe}(\text{CN})_6]$  solution yields reddish-brown  $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ .



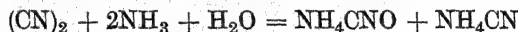
If copper is absent, passage of  $\text{H}_2\text{S}$  into the solution of the complex salt precipitates  $\text{CdS}$ , the final reaction being:



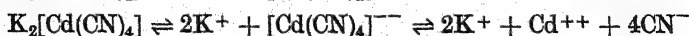
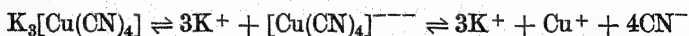
If copper is present, the addition of excess of  $\text{KCN}$  solution converts the ammine complexes into the colourless complex cyanides, potassium cuprocyanide  $\text{K}_3[\text{Cu}(\text{CN})_4]$  and potassium cadmiocyanide  $\text{K}_2[\text{Cd}(\text{CN})_4]$ .



the cyanogen produced reacts with the solution:



With potassium cuprocyanide, the concentration of the cuprous ions produced by the secondary ionisation of the complex ion  $[\text{Cu}(\text{CN})_4]^{--}$  is insufficient to exceed the solubility product of  $\text{Cu}_2\text{S}$  upon the addition of  $\text{H}_2\text{S}$ ; no precipitation therefore occurs. Potassium cadmiocyanide, on the other hand, is relatively unstable (compare Section I, 20) and the concentration of cadmium ions arising from the secondary dissociation of the  $[\text{Cd}(\text{CN})_4]^{--}$  is sufficient to exceed the solubility product of  $\text{CdS}$  when  $\text{H}_2\text{S}$  is passed into the solution.





## VII, 11. Table VI.—Analysis of Group IIB (Arsenic Group)

*Method A*

Treat the yellow ammonium sulphide extract of the Group II ppt. (see Table IV) with dilute HCl, with constant stirring, until it is slightly acid (test with litmus paper), warm and shake or stir for 1–2 minutes. A fine white or yellow ppt. is sulphur only. A yellow or orange flocculent ppt. indicates As, Sb and/or Sn present.\* Filter and wash the ppt., which may contain  $As_2S_5$ ,  $As_2S_3$ ,  $Sb_2S_5$ ,  $SnS_2$  and S, with a little  $H_2S$  water; reject the washings.

Transfer the ppt. to a small conical flask, add 5–10 ml. of concentrated HCl and boil gently for 5 minutes (with funnel in mouth of flask). Dilute with 2–3 ml. of water, pass  $H_2S$  for 1 minute to reprecipitate small amounts of arsenic that may have dissolved, and filter.

**Residue.** May contain  $As_2S_3$  (and/or  $As_2S_5$ ) + S: yellow.

Dissolve the ppt. in 3–4 ml. of warm dilute  $NH_3$  solution, filter (if necessary), add 3–4 ml. of 3%  $H_2O_2$  solution and warm for a few minutes to oxidise arsenite to arsenate. Add a few ml. of the  $Mg(NO_3)_2$  reagent. Stir and allow to stand. White, crystalline ppt. of  $Mg(NH_4)AsO_4 \cdot 6H_2O$ .

**As present.†**

Confirm as follows. Filter off ppt., and pour 1 ml. of  $AgNO_3$  solution containing 6–7 drops of 2N acetic acid on to residue on filter. Brownish-red residue of  $Ag_3AsO_4$ .

**Filtrate.** May contain  $H[SbCl_4]$  and  $H_2[SnCl_4]$ . Boil to expel  $H_2S$ , and divide the cold solution into three parts.

(i) Render just alkaline with dilute  $NH_3$  solution, disregard any slight ppt., add 1–2 grams of solid oxalic acid, boil and pass  $H_2S$  for ca. 1 minute into the hot filtrate.

Orange ppt. of  $Sb_2S_3$ .

**Sb present.**

(ii) To 2 drops of the solution on a spot plate, add a minute crystal of  $NaNO_2$  and then 2 drops of Rhodamine-B reagent.

Violet solution or ppt.

**Sb present.**

(iii) Partially neutralise the liquid, add 10 cm. of clean iron wire to 1 ml. of the solution. (If much Sb is present, it is better to reduce with Mg powder.) Warm gently to reduce the tin to the stannous state, and filter into a solution of  $HgCl_2$ .

White ppt. of  $Hg_2Cl_2$  or grey ppt. of Hg.

**Sn present.†**

(iv) Treat 0.2–0.3 ml. of the solution with 5–10 mg. of Mg powder, add 2 drops of  $FeCl_3$  solution, 2–3 drops of 5% tartaric acid solution, 1–2 drops of dimethylglyoxime reagent and then dilute  $NH_3$  solution until basic. Red coloration.

**Sn present.†**

*Explanation (Table VI)*

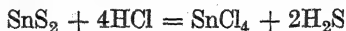
The precipitate obtained upon acidifying the ammonium sulphide  $(NH_4)_2S$  extract may contain  $As_2S_5$  (and/or  $As_2S_3$ ),

\* If Cu is present in the original Group II ppt., a small amount may be dissolved by the ammonium sulphide solution and re-precipitate here (brownish-red).

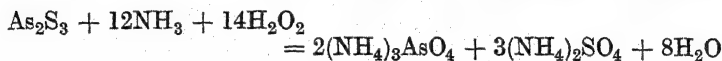
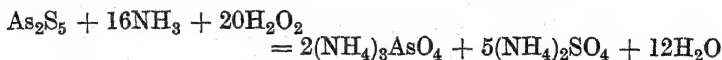
† If As or Sn is found, the original solution must be tested to ascertain whether present in the -ous or -ic state.

$\text{Sb}_2\text{S}_5$ ,  $\text{SnS}_2$  and  $\text{S}$ . Their separation depends upon the following facts:

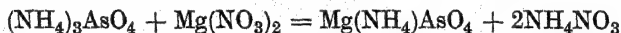
(1)  $\text{As}_2\text{S}_5$  is almost unaffected by concentrated  $\text{HCl}$ , whilst  $\text{Sb}_2\text{S}_5$  and  $\text{SnS}_2$  dissolve forming chlorides:



(2) The  $\text{As}_2\text{S}_5$  and/or  $\text{As}_2\text{S}_3$  is converted by ammoniacal  $\text{H}_2\text{O}_2$  solution into arsenate:

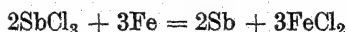
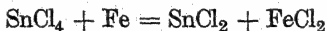


The arsenate is readily identified with the  $\text{Mg}(\text{NO}_3)_2$  reagent or with magnesia mixture as the crystalline  $\text{Mg}(\text{NH}_4)\text{AsO}_4 \cdot 6\text{H}_2\text{O}$ :



(3) The filtrate from the  $\text{HCl}$  treatment contains  $\text{SbCl}_3$  (or  $\text{H}[\text{SbCl}_4]$ ) and  $\text{SnCl}_4$  (or  $\text{H}_2[\text{SnCl}_6]$ ). Antimony is identified by adding  $\text{NH}_3$  solution and a large excess of oxalic acid to the mixture: a relatively stable tin-oxalate complex ion is formed. The antimony-oxalate complex ion is less stable and an appreciable concentration of  $\text{Sb}^{+++}$  ions is present in solution. Hence when  $\text{H}_2\text{S}$  is passed into the solution,  $\text{Sb}_2\text{S}_3$  alone is precipitated. Continued treatment with  $\text{H}_2\text{S}$  (beyond 3–5 minutes) may, however, result in the decomposition of the tin-oxalate complex ion: this will be indicated by the darkening of the orange  $\text{Sb}_2\text{S}_3$  precipitate. Antimony is also identified by the characteristic reaction with Rhodamine-B (Section III, 14, reaction 7).

(4) The addition of metallic iron to the diluted solution reduces the  $\text{SnCl}_4$  to  $\text{SnCl}_2$  and the  $\text{SbCl}_3$  to black  $\text{Sb}$ ; upon filtration, the solution contains  $\text{SnCl}_2$  and is free from  $\text{Sb}$ . The  $\text{SnCl}_2$  is identified by the usual reaction with  $\text{HgCl}_2$  solution; the  $\text{FeCl}_2$  produced has no action upon the  $\text{HgCl}_2$ .



The tin may also be identified by the dimethylglyoxime test (Section III, 16, reaction 6).

# VII, 11. Table VIA.—Analysis of Group IIB (Arsenic Group)

## Method B

The filtrate from the Copper Group (KOH extract) may contain  $\text{KAsO}_2$ ,  $\text{KAsS}_2$ ,  $\text{KSbO}_2$ ,  $\text{KSbS}_2$ ,  $\text{K}_2\text{SnO}_3$  or  $\text{K}_2[\text{Sn}(\text{OH})_6]$ ,  $\text{K}_2\text{SnS}_3$  and a little  $\text{K}_2[\text{HgS}_2]$ . Add concentrated  $\text{HCl}$  cautiously (dropwise and with cautious stirring) until the solution is distinctly acid to litmus paper. Treat with  $\text{H}_2\text{S}$  for 2–3 minutes to ensure complete precipitation of the sulphides. The formation of a ppt. indicates the possible presence of  $\text{HgS}$ ,  $\text{As}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_3$  and  $\text{SnS}_2$ . Filter; wash the ppt. with a little water and discard the washings. Transfer the ppt. to a small conical flask, add 5–10 ml. of concentrated  $\text{HCl}$ , heat to boiling [FUME CUPBOARD] and maintain the mixture near the boiling point over a free flame for 3–5 minutes; stir constantly. Dilute with a little water and filter.

**Residue.** May contain  $\text{HgS}$  and  $\text{As}_2\text{S}_3$ . If yellow, only  $\text{As}_2\text{S}_3$  present. Wash with water. Pour 5 ml. of dilute  $\text{NH}_3$  solution through the filter 2 or 3 times.

**Residue.**  
If dark-  
coloured  
( $\text{HgS}$ ).

**Hg present.**  
Confirm  
as in Table  
V, if Hg  
not found  
in Group  
IIA.

**Filtrate.** Add dilute  $\text{HNO}_3$  until distinctly acid.

Yellow ppt. of  $\text{As}_2\text{S}_3$ .  
**As present.†**

Confirm by redissolving ppt. in 3–4 ml. of warm, dilute  $\text{NH}_3$  solution, add 3–4 ml. of 3%  $\text{H}_2\text{O}_2$  solution and warm for a few minutes to oxidise arsenite to arsenate. Add a few ml. of  $\text{Mg}(\text{NO}_3)_2$  reagent, stir and allow to stand. White ppt. of  $\text{Mg}(\text{NH}_4)\text{AsO}_4 \cdot 6\text{H}_2\text{O}$ . Pour on the filter 1 ml. of  $\text{AgNO}_3$  solution containing 6–7 drops of 2N acetic acid. Brownish-red residue of  $\text{Ag}_3\text{AsO}_4$ .

**Filtrate.** May contain  $\text{H}[\text{SbCl}_4]$  and  $\text{H}_2[\text{SnCl}_4]$ . Divide into three parts.

(i) Render just alkaline with dilute  $\text{NH}_3$  solution, disregard any slight ppt., add 1–2 grams of solid oxalic acid, boil and pass  $\text{H}_2\text{S}$  for ca. 1 minute into the hot solution.

Orange ppt. of  $\text{Sb}_2\text{S}_3$ .

**Sb present.**

(ii) To 2 drops of the solution on a spot plate, add a minute crystal of  $\text{NaNO}_2$  and then 2 drops of Rhodamine-B reagent.

Violet ppt. or solution.

**Sb present.†**

(iii) Partially neutralise the liquid, add 10 cm. of clean iron wire to 1 ml. of the solution. (If much Sb is present, it is better to reduce with Mg powder.) Warm gently to reduce the tin to the stannous state, and filter into a solution of  $\text{HgCl}_2$ .

White ppt. of  $\text{Hg}_2\text{Cl}_2$  or grey ppt. of Hg.

**Sn present.†**

(iv) Treat 0.2–0.3 ml. of the solution with 5–10 mg. of Mg powder, add 2 drops of  $\text{FeCl}_3$  solution, 2–3 drops of 5% tartaric acid solution, 1–2 drops of dimethylglyoxime reagent, and then dilute  $\text{NH}_3$  solution until basic.

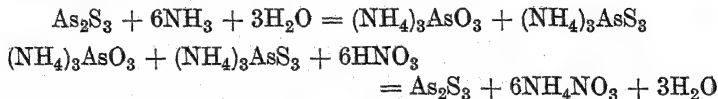
Red coloration.

**Sn present.**

† If As or Sn is found, the original solution must be tested to ascertain whether present in the -ous or -ic state.

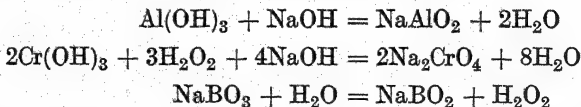
*Explanation (Table VIA)*

The precipitate obtained upon acidifying the KOH extract may contain  $\text{As}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{SnS}_2$  and a little  $\text{HgS}$  (for equations, see *Explanation* to Table IVA). The basis of the subsequent steps is similar to that described for Table VI with the variation that  $\text{HgS}$  may accompany the  $\text{As}_2\text{S}_3$  precipitate. These two sulphides are readily separated by utilising the fact that  $\text{As}_2\text{S}_3$  alone is soluble in  $\text{NH}_3$  solution; upon acidifying the ammoniacal extract, yellow  $\text{As}_2\text{S}_3$  is precipitated.

*Explanation (Table VII)*

The precipitate may contain  $\text{Fe}(\text{OH})_3$ ,  $\text{Cr}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_3$  and a little  $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ : Co, Ni, Zn and some Mn remain in solution as the complex ammine ions. {The  $\text{MnO}_2 \cdot x\text{H}_2\text{O}$  owes its formation to oxidation of some  $\text{Mn}(\text{OH})_2$  (which is held in solution by  $\text{NH}_4\text{Cl}$  and aqueous  $\text{NH}_3$ ) by air and also partially to the  $\text{HNO}_3$  or  $\text{Br}_2$  water treatment made primarily to oxidise  $\text{Fe}^{++}$  to  $\text{Fe}^{+++}$ ; some  $\text{Mn}^{++}$  is simultaneously oxidised to  $\text{Mn}^{++++}$  and the latter is precipitated as  $\text{MnO}_2 \cdot x\text{H}_2\text{O}$  by the group reagent.} The separation is based upon the following facts:

(1) When the precipitate is boiled with  $\text{NaOH}$  and  $\text{H}_2\text{O}_2$  solution (or with  $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$  solution), the  $\text{Al}(\text{OH})_3$  is converted into the soluble sodium aluminate  $\text{NaAlO}_2$  and the  $\text{Cr}(\text{OH})_3$  is oxidised to the yellow, soluble sodium chromate  $\text{Na}_2\text{CrO}_4$ . The  $\text{Fe}(\text{OH})_3$  and  $\text{MnO}_2 \cdot x\text{H}_2\text{O}$  remain undissolved. The excess of  $\text{H}_2\text{O}_2$  is decomposed upon boiling: any reduction of chromate upon acidification is thus avoided.



The tests for Cr in the yellow solution of  $\text{Na}_2\text{CrO}_4$  include the precipitation of  $\text{PbCrO}_4$  with acetic acid and lead acetate solution (Section IV, 33, reaction 3) and the formation of "perchromic acid," best in the presence of a little amyl alcohol (Section IV, 33, reaction 4).

Aluminium is identified by reprecipitation as  $\text{Al}(\text{OH})_3$  by

## VII, 12. Table VII.—Analysis of Group IIIA (Iron Group)\*

The ppt. produced by adding  $\text{NH}_4\text{Cl}$  and  $\text{NH}_3$  solution may contain  $\text{Fe}(\text{OH})_3$ ,  $\text{Cr}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_3$  and a little  $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ . Wash with a little hot 1%  $\text{NH}_4\text{Cl}$  solution. Transfer the ppt. with the aid of 5–10 ml. of water to a small evaporating basin or a small beaker, add 1–1.5 grams of sodium perborate  $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$  (or add 5 ml. of  $\text{NaOH}$  solution, followed by 5 ml. of 3%  $\text{H}_2\text{O}_2$  solution). Boil gently until the evolution of  $\text{O}_2$  ceases (2–3 minutes). Filter.

**Residue.** May contain  $\text{Fe}(\text{OH})_3$  and  $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ .

Wash with a little hot water.

Dissolve a small portion of the ppt. in 1 ml. of dilute  $\text{HNO}_3$  (1 : 1) with the aid (if necessary) of 3–4 drops of 3%  $\text{H}_2\text{O}_2$  solution or 1 drop of saturated  $\text{H}_2\text{SO}_3$  solution. Boil (to decompose  $\text{H}_2\text{O}_2$ ), cool thoroughly, add 0.05–0.1 gram of sodium bismuthate, shake and allow the solid to settle.

Violet solution of  $\text{HMnO}_4$ .

**Mn present.**

Dissolve another portion of the ppt. in dilute  $\text{HCl}$  (filter, if necessary).

*Either*—Add a few drops of  $\text{KSCN}$  solution.

Deep red coloration.

**Fe present.**

*Or*—Add  $\text{K}_4[\text{Fe}(\text{CN})_6]$  solution.

Blue ppt.

**Fe present.**

The original solution or substance should be tested with  $\text{K}_4[\text{Fe}(\text{CN})_6]$  and with  $\text{KSCN}$  to determine whether  $\text{Fe}^{++}$  or  $\text{Fe}^{+++}$ .

**Filtrate.** May contain  $\text{Na}_2\text{CrO}_4$  (yellow) and/or  $\text{NaAlO}_2$  (colourless).

If colourless, Cr is absent and need not be considered further.

If the solution is yellow, Cr is indicated.

Divide the liquid into three portions.

(i) Acidify with acetic acid and add lead acetate solution.

Yellow ppt. of  $\text{PbCrO}_4$ .

**Cr present.**

(ii) Acidify 2 ml. with dilute  $\text{HNO}_3$ , cool thoroughly, add 1 ml. of amyl alcohol, and 4 drops of 3%  $\text{H}_2\text{O}_2$  solution. Shake well and allow the two layers to separate.

Blue upper layer (containing "perchromic acid"; it does not keep well).

**Cr present.**

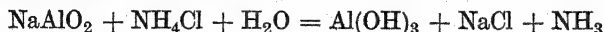
(iii) Acidify with dilute  $\text{HCl}$  (test with litmus paper), then add dilute  $\text{NH}_3$  solution until just alkaline. Heat to boiling. Filter.

White gelatinous ppt. of  $\text{Al}(\text{OH})_3$ .

**Al present.**

Dissolve a small portion of the ppt. in 1 ml. of hot dilute  $\text{HCl}$ . Cool, add 1 ml. of 10% ammonium acetate solution and 0.5 ml. of the "aluminon" reagent. Stir the solution and render basic with ammonium carbonate solution. A red ppt. confirms the presence of Al.

boiling in the presence of  $\text{NH}_4\text{Cl}$  and by the "aluminon" test (Section III, 21, reaction 7).



(2) The precipitate ( $\text{Fe}(\text{OH})_3 + \text{MnO}_2 \cdot x\text{H}_2\text{O}$ ), remaining after boiling with  $\text{NaOH} + \text{H}_2\text{O}_2$  or with  $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ , is tested portionwise for Fe and Mn. Extraction with dilute  $\text{HCl}$  dissolves the  $\text{Fe}(\text{OH})_3$  as  $\text{FeCl}_3$ : the solution may be treated

\* The removal of interfering acid radicals (organic acids, borates, fluorides, silicates and phosphates) has been described in Tables I and II; see also Chapter VIII.

with  $K_4[Fe(CN)_6]$  or with KSCN solution (Section III, 20, reactions 5 and 10) and the presence of Fe established.

Another portion of the precipitate is dissolved in dilute  $HNO_3$  and a few drops of  $H_2O_2$  solution:



and the  $Mn^{++}$  is oxidised to permanganic acid  $HMnO_4$  with sodium bismuthate  $NaBiO_3$  (Section III, 26, reaction 7) or with  $PbO_2$  and  $HNO_3$  (Section III, 26, reaction 5).

### VII, 13. Table VIII.—Analysis of Group IIIB (Zinc Group)

#### Method A

The ppt. may contain  $CoS$ ,  $NiS$ ,  $MnS$  and  $ZnS$ . Wash well with 1%  $NH_4Cl$  solution to which 1% by volume of  $(NH_4)_2S$  has been added; reject the washings. Transfer the ppt. to a small beaker. Add 10 ml. of  $N$   $HCl$  (1 volume of concentrated acid: 11–12 volumes of water), stir well, allow to stand for 2–3 minutes and filter.

**Residue.** If black, may contain  $CoS$  and  $NiS$ . Test residue with borax bead. If blue,  $Co$  is indicated.

Dissolve the ppt. in a mixture of 1.5 ml. of 10%  $NaOCl$  solution and 0.5 ml. of dilute  $HCl$ . Add 1 ml. of dilute  $HCl$ , and boil until all  $Cl_2$  is expelled. Cool and dilute to about 4 ml.

Divide the solution into two equal parts.

(i) Add 1 ml. of amyl alcohol, 2 grams of solid  $NH_4SCN$  and shake well. Amyl alcohol layer coloured blue.

**Co present.**

(ii) Add 2 ml. of  $NH_4Cl$  solution,  $NH_3$  solution until alkaline, and then excess of dimethylglyoxime reagent.

Red ppt.

**Ni present.**

**Filtrate.** May contain  $MnCl_2$  and  $ZnCl_2$  and, possibly, traces of  $CoCl_2$  and  $NiCl_2$ . Boil until  $H_2S$  removed (test with lead acetate paper), cool, add excess of  $NaOH$  solution, followed by 1 ml. of 3%  $H_2O_2$  solution. Boil for 3 minutes. Filter.

**Residue.** Largely  $MnO_2 \cdot xH_2O$  and perhaps traces of  $Ni(OH)_2$  and  $Co(OH)_3$  (1). Dissolve the ppt. in 5 ml. of dilute  $HNO_3$  (1 : 1) with the addition of a few drops of 3%  $H_2O_2$  solution, if necessary (2). Boil to decompose excess of  $H_2O_2$  and cool. Add 0.05 gram of sodium bismuthate, stir and allow to settle. Purple solution of  $HMnO_4$ .

**Mn present.**

**Filtrate.** May contain  $Na_2[ZnO_2]$ . Divide into two parts.

(1) Acidify with acetic acid and pass  $H_2S$ . White ppt. of  $ZnS$ .

**Zn present.**

(ii) Just acidify with dilute  $H_2SO_4$ , add 0.5 ml. of 0.1% cobalt acetate solution and 0.5 ml. of the ammonium mercuri-thiocyanate reagent: stir.

Pale blue ppt.

**Zn present.**

**Notes.** (1) The  $Mn$  may be separated, if desired, from any  $Co$  or  $Ni$  by reprecipitating as  $MnO_2$  in ammoniacal solution. To the nitric acid solution  $\{MnO_2 + 2HNO_3 + H_2O_2 = Mn(NO_3)_2 +$

$\text{O}_2 + 2\text{H}_2\text{O}$ }, add 5 ml. of  $\text{NH}_4\text{Cl}$  solution and about 5 ml. excess of dilute aqueous  $\text{NH}_3$ . Then add 1 gram of solid  $\text{K}_2\text{S}_2\text{O}_8$ , boil for 30 seconds, filter and wash. The Co and Ni remain in solution as  $[\text{Co}(\text{NH}_3)_6]^{+++}$  and  $[\text{Ni}(\text{NH}_3)_6]^{++}$ . The  $\text{MnO}_2$  may be filtered off, dissolved in  $\text{HNO}_3 + \text{H}_2\text{O}_2$ , etc. This separation is not essential.

(2) Any  $\text{Ni}(\text{OH})_2$  and  $\text{Co}(\text{OH})_3$  present will dissolve in the  $\text{HNO}_3 + \text{H}_2\text{O}_2$  to form  $\text{Ni}(\text{NO}_3)_2$  and  $\text{Co}(\text{NO}_3)_2$  respectively. They dissolve less readily than  $\text{MnO}_2$ , so that if any difficulty is experienced in effecting complete solution of the precipitate, the undissolved solid may be discarded and the clear solution used to test for Mn.

### Explanation (Table VIII)

The separation of NiS, CoS, MnS and ZnS, which may be contained in the precipitate, is based upon the following facts:

(1) MnS and ZnS dissolve readily in cold, very dilute (*ca. N*) HCl, whilst NiS and CoS dissolve only slightly during the short period (2-3 minutes) that the sulphides are in contact with the acid.



The presence of small amounts of  $\text{Ni}^{++}$  and  $\text{Co}^{++}$  ions in the filtrate (containing  $\text{Mn}^{++}$  and  $\text{Zn}^{++}$  ions) causes no serious interference in the subsequent tests.

(2) The detection of Co and of Ni in a mixture of CoS and NiS is carried out upon separate portions of the solution prepared by dissolving the sulphides in aqua regia or in a mixture of NaOCl solution and dilute HCl:



The tests employed are highly sensitive; moderate quantities of other elements do not interfere and separation is therefore unnecessary.

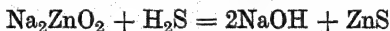
The  $\text{NH}_4\text{SCN}$  test for Co depends upon the formation of the blue ammonium cobaltothiocyanate  $(\text{NH}_4)_2[\text{Co}(\text{SCN})_4]$  or of the free acid  $\text{H}_2[\text{Co}(\text{SCN})_4]$  (in the presence of HCl), which dissolve and are comparatively stable in amyl alcohol. The disturbing effect of iron (due to the red  $[\text{Fe}(\text{SCN})]^{++}$ ), may be eliminated by the addition of a soluble fluoride when the complex and highly stable ferrifluoride ion  $[\text{FeF}_6]^{---}$  is formed (Section III, 24, reaction 6).

The dimethylglyoxime test for Ni (Section III, 25, reaction 8) is applicable in the presence of Co provided excess of the reagent is added.

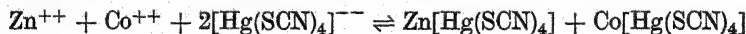
(3) The solution containing  $\text{MnCl}_2$  and  $\text{ZnCl}_2$  and possibly traces of  $\text{CoCl}_2$  and  $\text{NiCl}_2$  is boiled to remove  $\text{H}_2\text{S}$ , and then warmed with a little  $\text{H}_2\text{O}_2$  solution to oxidise the  $\text{Co}^{++}$  to  $\text{Co}^{+++}$  and the  $\text{Mn}^{++}$  to  $\text{Mn}^{++++}$ :  $\text{Co}(\text{OH})_2$  is slightly soluble but  $\text{Co}(\text{OH})_3$  is insoluble in excess of  $\text{NaOH}$  solution. Upon adding excess of  $\text{NaOH}$  solution, the  $\text{Zn}(\text{OH})_2$  precipitated initially will dissolve to form sodium zincate  $\text{Na}_2[\text{ZnO}_2]$ , whilst  $\text{MnO}_2 \cdot x\text{H}_2\text{O}$  and traces of  $\text{Ni}(\text{OH})_2$  and  $\text{Co}(\text{OH})_3$  will be precipitated.

The Mn is readily identified in the precipitate by dissolving it in dilute  $\text{HNO}_3$  and a little  $\text{H}_2\text{O}_2$  and applying the sodium bismuthate test (see *Explanation* to Table VII).

The Zn may be identified as white  $\text{ZnS}$  by passing  $\text{H}_2\text{S}$  into the  $\text{NaOH}$  extract as such or acidified with acetic acid:



A characteristic test for Zn is the mercuri-thiocyanate reaction with a small amount of  $\text{Co}(\text{NO}_3)_2$  solution and the ammonium mercuri-thiocyanate reagent. A pale blue precipitate is formed (which may be readily detected by shaking with a little amyl alcohol). This is due to coprecipitation of the cobalt complex with that of zinc (Section III, 27, reaction 9):



Zinc ions, if present alone, give a *white* precipitate. With traces of copper salts, a blue-violet precipitate forms.



## VII, 13. Table VIIIA.—Analysis of Group IIIB (Zinc Group)

## Method B

The ppt. may contain  $\text{CoS}$ ,  $\text{NiS}$ ,  $\text{MnS}$  and  $\text{ZnS}$ . Wash well with 1%  $\text{NH}_4\text{Cl}$  solution to which 1% by volume of yellow ammonium sulphide solution has been added; reject the washings. Transfer the ppt. to a porcelain basin, add 5 ml. of water and 5 ml. of concentrated  $\text{HCl}$  and stir for 2–3 minutes. If a black residue is obtained, the presence of  $\text{NiS}$  and  $\text{CoS}$  is indicated: if complete solution takes place, only small amounts of  $\text{Ni}$  and  $\text{Co}$  are likely to be present. Evaporate the mixture to 2–3 ml. in the *FUME CUPBOARD*, add 4 ml. of concentrated  $\text{HNO}_3$  (1) and concentrate to 2–3 ml. If the solution is not clear, dilute with 8–10 ml. of water, filter off the sulphur and return the filtrate to the porcelain basin in the fume cupboard. Boil down to 1–2 ml., taking great care not to evaporate to dryness. Add 5 ml. of concentrated  $\text{HNO}_3$  and evaporate again to 1–2 ml. (2).

Remove about 0.2 ml. of the solution with the aid of a dropper to a small test-tube, add 5 ml. of dilute  $\text{HNO}_3$  and then 0.1 gram of sodium bismuthate; stir and allow to stand. A purple coloration, due to  $\text{HMnO}_4$ , indicates **Mn present**. If  $\text{Mn}$  is present, treat the remainder of the solution in the porcelain basin in accordance with the procedure commencing at (A); if  $\text{Mn}$  is absent, continue the analysis from (B) onwards.

(A) Add 10–15 ml. of concentrated  $\text{HNO}_3$ , and heat just to boiling in the fume cupboard. By means of a spatula (preferably of glass), add finely-powdered  $\text{KClO}_3$  in 0.1 gram portions [*GREAT CARE: DANGER OF EXPLOSION* (3)]; after each addition boil gently until the greenish-yellow vapours of chlorine dioxide are expelled. Continue the addition of 0.1 gram portions, boiling gently after each addition, until 1.5 grams have been added. A brown or black ppt. of hydrated  $\text{MnO}_2$  will form. Dilute with 3 ml. of water. Filter the ppt. through a small sintered glass funnel or crucible, and wash the ppt. with 2–3 ml. of water.

**Residue.**  
 $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ .

**Filtrate.** Evaporate in a porcelain basin [*FUME CUPBOARD*] to 2–3 ml. Allow to cool.

(B) Dilute with 5 ml. of water. Add excess of  $\text{NaOH}$  solution and 1 ml. of 3%  $\text{H}_2\text{O}_2$  solution (4). Boil for 3 minutes and filter.

**Residue.** May contain  $\text{Ni}(\text{OH})_2$  and  $\text{Co}(\text{OH})_3$ .

Dissolve the ppt. in dilute  $\text{HCl}$ , and test for  $\text{Co}$  and  $\text{Ni}$  as detailed in Table VIII.

**Filtrate.** May contain  $\text{Na}_2\text{ZnO}_2$ .

Test for  $\text{Zn}$  as detailed in Table VIII.

**Notes.** (1) The precipitate is first treated with dilute  $\text{HCl}$  alone, partly to indicate the presence of  $\text{Ni}$  and  $\text{Co}$  in quantity but also because much free sulphur and sulphate would be formed if an oxidising agent were used with the  $\text{HCl}$  at this stage.

(2) The repeated evaporation with concentrated  $\text{HNO}_3$  completely removes chloride ion, which interferes with the subsequent precipitation of  $\text{MnO}_2$ .

(3) The action of  $\text{KClO}_3$  in concentrated  $\text{HNO}_3$  is rapid and vigorous, and one of the decomposition products is the explosive,

greenish-yellow gas  $\text{ClO}_2$ . If the chlorate is added in small quantities as instructed and the solution is boiled gently between each addition to prevent the accumulation of  $\text{ClO}_2$ , the procedure is reasonably safe and the only evidence of explosion will be a gentle puff of gas. Under no circumstances may more than 0.1 gram of  $\text{KClO}_3$  be added at one time.

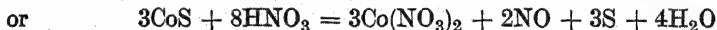
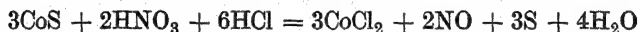
(4) The  $\text{H}_2\text{O}_2$  solution is added to ensure the complete precipitation of cobalt as cobaltic hydroxide  $\text{Co}(\text{OH})_3$ , since cobaltous hydroxide is slightly soluble in excess of  $\text{NaOH}$  solution.

### *Explanation (Table VIIIA)*

The salient facts in the separation of the elements in Group IIIB are:

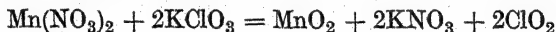
(1) The addition of dilute  $\text{HCl}$  to the group precipitate will serve to indicate the presence of  $\text{Co}$  and  $\text{Ni}$  in quantity since  $\text{CoS}$  and  $\text{NiS}$  do not dissolve appreciably in the cold.

(2) Boiling of the undissolved sulphides with  $\text{HCl}$  in the presence of concentrated  $\text{HNO}_3$  or with concentrated  $\text{HNO}_3$  alone results in the solution of the sulphides and the separation of sulphur:



If the action of concentrated  $\text{HNO}_3$  is continued, the  $\text{S}$  will gradually pass into solution as  $\text{H}_2\text{SO}_4$ .

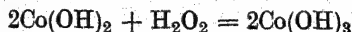
(3) The  $\text{Mn}$  is first precipitated from a concentrated  $\text{HNO}_3$  solution by means of  $\text{KClO}_3$ :



(4) In the subsequent separation of  $\text{Ni}$ ,  $\text{Co}$  and  $\text{Zn}$ , the addition of excess of  $\text{NaOH}$  solution will yield a precipitate of cobaltous and nickelous hydroxides and a solution of sodium zincate:



Cobaltous hydroxide is slightly soluble in alkali hydroxide solution. The addition of a peroxide (or of bromine water) oxidises it to cobaltic hydroxide, which is precipitated quantitatively:



## VII, 14. Table IX.—Analysis of Group IV (Calcium Group)

## Method A

The ppt. may contain  $\text{BaCO}_3$ ,  $\text{SrCO}_3$  and  $\text{CaCO}_3$ . Wash with a little hot water and reject the washings. Dissolve the ppt. in 5 ml. of hot 2N acetic acid by pouring the acid repeatedly through the filter paper. Test 1 ml. for barium by adding  $\text{K}_2\text{CrO}_4$  solution dropwise to the nearly boiling solution. A yellow ppt. indicates Ba.

**Ba present.** Heat the remainder of the solution almost to boiling and add a slight excess of  $\text{K}_2\text{CrO}_4$  solution (i.e. until the solution assumes a yellow colour and precipitation is complete). Filter and wash the ppt. (C) with a little hot water. Render the hot filtrate and washings basic with  $\text{NH}_3$  solution and add an excess of  $(\text{NH}_4)_2\text{CO}_3$  solution or, better, a little solid  $\text{Na}_2\text{CO}_3$ . A white ppt. indicates the presence of  $\text{SrCO}_3$  and/or  $\text{CaCO}_3$ . Wash the ppt. with hot water, and dissolve it in 4 ml. of warm 2N acetic acid: boil to remove excess of  $\text{CO}_2$  (solution A).

**Ba absent.** Discard the portion used in testing for barium, and employ the remainder of the solution (B), after boiling for 1 minute to expel  $\text{CO}_2$ , to test for strontium and calcium.

**Residue (C).**  
Yellow:  $\text{BaCrO}_4$ .

Wash well with hot water. Dissolve the ppt. in a little concentrated HCl, evaporate almost to dryness and apply the flame test.

Green (or yellowish-green) flame.

**Ba present.**  
(Use spectro-scope, if available.)

**Solution A or Solution B.** The volume should be about 4 ml.

*Either*—To 2 ml. of the cold solution, add 2 ml. of saturated  $(\text{NH}_4)_2\text{SO}_4$  solution, followed by 0.2 gram of sodium thiosulphate, heat in a beaker of boiling water for 5 minutes and allow to stand for 1–2 minutes. Filter.

*Or*—To 2 ml. of the solution add 2 ml. of triethanolamine, 2 ml. of saturated  $(\text{NH}_4)_2\text{SO}_4$  solution, heat on a boiling water bath with continuous stirring for 5 minutes and allow to stand for 1–2 minutes. Dilute with an equal volume of water and filter.

**Residue.** Largely  $\text{SrSO}_4$ . Wash with a little water. Transfer ppt. and filter paper to a small crucible, heat until ppt. has charred (or burn filter paper and ppt., held in a Pt wire, over a crucible), moisten ash with a few drops of concentrated HCl and apply the flame test.

Crimson flame.

**Sr present.**  
(Use spectro-scope, if available.)

**Filtrate.** May contain Ca complex.

(If Sr is absent, use 2 ml. of solution A or B.) Add a little  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution\* and warm on a water bath.

White ppt. of  $\text{CaC}_2\text{O}_4$ .

**Ca present.**†

Confirm by flame test on ppt.—brick-red flame.

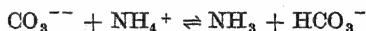
(Use spectro-scope, if available.)

\* When triethanolamine has been used in the separation, acidification with dilute acetic acid may assist the precipitation of the  $\text{CaC}_2\text{O}_4$ .

† The following is an alternative test for Ca. Place a drop or two of the filtrate upon a glass slide, add a drop or two of dilute  $\text{H}_2\text{SO}_4$ , and concentrate by placing the slide on a small crucible and warming until crystallisation just commences. Examine the crystals in a microscope (magnification: ca. 100×). Bundles of needles or elongated prisms. **Ca present.**

*Explanation (Table IX)*

The reasons for evaporating the filtrate from Group IIIB to dryness, eliminating ammonium salts and then dissolving the residue in dilute HCl before precipitating with excess of  $(\text{NH}_4)_2\text{CO}_3$  in the presence of a little  $\text{NH}_4\text{Cl}$  and aqueous  $\text{NH}_3$ , have been given in detail at the end of Section III, 31. Essentially, the  $\text{CO}_3^{--}$  ion concentration is reduced by the high concentration of  $\text{NH}_4^+$  ions present in the solution so that, unless the latter are removed, precipitation of  $\text{BaCO}_3$ ,  $\text{SrCO}_3$  and  $\text{CaCO}_3$  is incomplete:



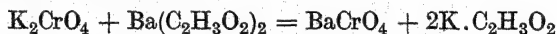
Magnesium is not precipitated either as  $\text{Mg}(\text{OH})_2$  (S.P.  $3.4 \times 10^{-11}$ ) or as  $\text{MgCO}_3$  (S.P.  $1.0 \times 10^{-5}$ ) since both the concentration of  $\text{OH}^-$  ions in the presence of  $\text{NH}_4\text{Cl}$  and the concentration of  $\text{CO}_3^{--}$  ions are such that the solubility products of the respective magnesium compounds are not exceeded. The solubility products of the carbonates constituting Group IV are:  $\text{BaCO}_3$ ,  $8.1 \times 10^{-9}$ ;  $\text{SrCO}_3$ ,  $1.6 \times 10^{-9}$ ; and  $\text{CaCO}_3$ ,  $4.8 \times 10^{-9}$ .

The precipitated carbonates are dissolved in dilute acetic acid forming solutions of the acetates:



The procedure described for separating the three elements utilises the following facts:

(1)  $\text{BaCrO}_4$  (S.P.  $1.6 \times 10^{-10}$ ) is almost insoluble in dilute acetic acid, whilst  $\text{SrCrO}_4$  (S.P.  $3.6 \times 10^{-5}$ ) and  $\text{CaCrO}_4$  (S.P.  $2.3 \times 10^{-2}$ ) are soluble and are therefore not precipitated in a dilute acetic acid medium.



The function of the acetic acid is to convert some of the  $\text{CrO}_4^{--}$  ions into  $\text{Cr}_2\text{O}_7^{--}$  ions, thus lowering the  $\text{CrO}_4^{--}$  ion concentration so that the solubility products of  $\text{SrCrO}_4$  and  $\text{CaCrO}_4$  are not attained and in consequence they remain in solution:



It will be realised that in the presence of a large  $\text{H}^+$  ion concentration (as distinct from the limited one due to the weak acetic acid), the  $[\text{CrO}_4^{--}]$  may be such that the S.P. of  $\text{BaCrO}_4$  is not reached and under such conditions  $\text{BaCrO}_4$  will not be precipitated: this accounts for the solubility of this salt in dilute mineral acids.

(2) Upon adding saturated  $(\text{NH}_4)_2\text{SO}_4$  solution and warming,  $\text{SrSO}_4$  is largely precipitated upon standing: the addition of

some  $\text{Na}_2\text{S}_2\text{O}_3$  increases the solubility of  $\text{CaSO}_4$  and this reduces the amount of coprecipitation with  $\text{SrSO}_4$ . The formation of a soluble complex salt, such as  $(\text{NH}_4)_2[\text{Ca}(\text{SO}_4)_2]$ , has been suggested to account for the failure of  $\text{CaSO}_4$  to precipitate in appreciable quantity with  $(\text{NH}_4)_2\text{SO}_4$  solution.

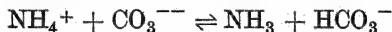
In the alternative procedure, using triethanolamine  $\text{N}(\text{C}_2\text{H}_4\text{OH})_3$  and saturated  $(\text{NH}_4)_2\text{SO}_4$  solution, it is probable that a calcium triethanolamine complex ion is formed and, in consequence, very little  $\text{CaSO}_4$  is precipitated: however, the concentration of  $\text{Ca}^{++}$  ions due to the dissociation of the complex ion is such that the solubility product of  $\text{CaC}_2\text{O}_4$  ( $2.6 \times 10^{-9}$ ) is exceeded upon adding  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution.

$\text{SrSO}_4$  does not give a flame coloration easily; it is therefore partially reduced to  $\text{SrS}$  by the carbon of the filter paper. Treatment of the residue containing  $\text{SrS}$  with  $\text{HCl}$  gives the relatively volatile  $\text{SrCl}_2$ .

(3) Calcium is readily identified by precipitation as  $\text{CaC}_2\text{O}_4$ , followed by the flame test (best observed through a spectro-scope). It may also be converted into  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , and the characteristic crystals examined in a microscope—magnification of about 100 diameters.

#### *Explanation (Table IXA)*

The barium is separated as  $\text{BaCrO}_4$  as in Table IX, and the strontium and barium are precipitated as carbonates by  $(\text{NH}_4)_2\text{CO}_3$  solution in the presence of a little aqueous ammonia. It is better to employ  $\text{Na}_2\text{CO}_3$  to precipitate the carbonates; the influence of ammonium salts in tending to reduce the carbonate ion concentration is thus eliminated:



The mixture of  $\text{SrCO}_3$  and  $\text{CaCO}_3$  is treated cautiously with 83 per cent  $\text{HNO}_3$ ; the carbonates are thus converted into the nitrates.  $\text{Sr}(\text{NO}_3)_2$  is insoluble in the medium whilst the  $\text{Ca}(\text{NO}_3)_2$  dissolves. The  $\text{Sr}(\text{NO}_3)_2$  is collected by filtration through a sintered glass crucible or funnel: the presence of Sr is confirmed by the flame test, preferably with the aid of a hand spectro-scope.

Upon gentle evaporation of the filtrate to remove  $\text{HNO}_3$ , the  $\text{Ca}(\text{NO}_3)_2$  is obtained. The latter is dissolved in water, rendered ammoniacal and then faintly acid with dilute acetic acid, and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution added whereupon  $\text{CaC}_2\text{O}_4$  is precipitated; the flame test may be applied to the  $\text{CaC}_2\text{O}_4$  precipitate. Alternatively, the calcium may be converted into

## VII, 14. Table IXA.—Analysis of Group IV (Calcium Group)

## Method B

The ppt. may contain  $\text{BaCO}_3$ ,  $\text{SrCO}_3$  and  $\text{CaCO}_3$ . Wash with a little hot water and reject the washings. Dissolve the ppt. in 5 ml. of hot 2N acetic acid by pouring the acid repeatedly through the filter paper. Test 1 ml. for barium by adding  $\text{K}_2\text{CrO}_4$  solution dropwise to the nearly boiling solution. A yellow ppt. indicates the presence of Ba.

**Ba present.** Heat the remainder of the solution almost to boiling and add a slight excess of  $\text{K}_2\text{CrO}_4$  solution (i.e. until precipitation is complete and the solution assumes a yellow colour). Filter and wash the ppt. (C) with a little hot water. Combine the filtrate and washings (solution A).

**Ba absent.** Discard the portion used in testing for barium, and employ the remainder of the solution (B), after boiling for 1 minute to expel  $\text{CO}_2$  to test for strontium and barium.

**Residue (C).**  
Yellow:  $\text{BaCrO}_4$ .

Wash well with hot water. Dissolve the ppt. in a little concentrated HCl, evaporate almost to dryness and apply the flame test. Green (or yellowish-green) flame.

**Ba present.**  
(Use spectro-scope, if available.)

**Solution A or Solution B.** Render alkaline with  $\text{NH}_3$  solution, and add a slight excess of  $(\text{NH}_4)_2\text{CO}_3$  solution or, better, a little solid  $\text{Na}_2\text{CO}_3$ . Place the test-tube in a boiling water bath for 5 minutes. A white ppt. indicates the presence of  $\text{SrCO}_3$  and/or  $\text{CaCO}_3$ . Filter and wash the precipitated carbonates with hot water until the washings are colourless: discard the washings. Drain the liquid from the ppt. as completely as possible. Transfer the ppt. to a small beaker, add cautiously 15–20 ml. of 83%  $\text{HNO}_3$ ,\* stir for 3–4 minutes with a glass rod and filter through a sintered glass crucible.

**Residue.**

White:

$\text{Sr}(\text{NO}_3)_2$ .

**Sr present.**

Confirm by flame test: crimson flame.

(Use spectro-scope, if available.)

**Filtrate.** May contain  $\text{Ca}(\text{NO}_3)_2$ . Transfer most of the liquid to a porcelain basin and evaporate *almost* to dryness [*FUME CUPBOARD*]. Dissolve the residue in 2 ml. of water (solution D), render alkaline with  $\text{NH}_3$  solution, then acid with dilute acetic acid, add excess of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution and warm on a water bath.

White ppt. of  $\text{CaC}_2\text{O}_4$ .

**Ca present.**

Filter off the ppt. and apply the flame test: brick-red flame.

(Use spectro-scope, if available.)

*Alternatively*—Place a drop or two of solution D on a glass slide, and add a drop or two of dilute  $\text{H}_2\text{SO}_4$ . Concentrate by placing the slide on a small crucible and warm until crystallisation just commences. Examine the crystals in a microscope (magnification, ca. 100×).

Bundles of needles or elongated prisms.

**Ca present.**

\* The 83 per cent  $\text{HNO}_3$  (in which  $\text{Sr}(\text{NO}_3)_2$  is insoluble) is prepared by adding 100 grams (68.0 ml.) of concentrated  $\text{HNO}_3$  (sp. gr. 1.42: ca. 70 per cent) to 100 grams (66.2 ml.) of fuming  $\text{HNO}_3$  (sp. gr. 1.5: ca. 95 per cent).

the sulphate  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , and the latter identified under the microscope.

The nitric acid procedure gives an excellent separation of strontium from calcium.

### VII, 15. Table X.—Analysis of Group V (Alkali Group)

Treat the dry residue from Group IV with 4 ml. of water, stir, warm for 1 minute and filter.†	
<p><b>Residue.</b> Dissolve in a few drops of dilute HCl and add 2–3 ml. of water. Divide the solution into two unequal parts.</p> <p>(i) <i>Larger portion*</i>: Treat 1 ml. of 2% oxine solution in 2N acetic acid with 4 ml. of 2.5N ammonia solution and, if necessary, warm to dissolve any precipitated oxine. Add a little <math>\text{NH}_4\text{Cl}</math> solution to the test solution, followed by the ammoniacal oxine reagent, and heat to the boiling point for 1–2 minutes (the odour of <math>\text{NH}_3</math> should be discernible).</p> <p>Pale yellow ppt. of Mg “oxinate.”  <b>Mg present.</b></p> <p>(ii) <i>Smaller portion</i>: To 3–4 drops, add 2 drops of the “magneson” reagent, followed by several drops of NaOH solution until alkaline. A blue ppt. confirms Mg.</p>	<p><b>Filtrate.</b> Divide into two parts (a) and (b).</p> <p>(a) Add a little uranyl magnesium acetate reagent, shake and allow to stand for a few minutes.</p> <p>Yellow crystalline ppt.  <b>Na present.</b></p> <p>Confirm by flame test: <i>persistent yellow flame.</i></p> <p>(b) Add a little sodium cobaltinitrite solution (or ca. 4 mg. of the solid) and a few drops of dilute acetic acid. Stir and, if necessary, allow to stand for 1–2 minutes.</p> <p>Yellow ppt. of <math>\text{K}_3[\text{Co}(\text{NO}_2)_6]</math>.  <b>K present.</b></p> <p>Confirm by flame test and view through two thicknesses of cobalt glass‡: red coloration (usually transient).</p>
<p><b>Examination for ammonium.</b> This has already been carried out with the original substance in the preliminary tests (Section VII, 2, test (v)).</p>	

#### Explanation (Table X)

The filtrate from Group IV may contain Mg, Na, K and ammonium salts. It is evaporated to dryness and heated until all the ammonium salts have been volatilised: a residue is indicative of the presence of one or more of these metals. The

\* If it is desired to carry out the less satisfactory  $\text{Na}_2\text{HPO}_4$  test for comparison with the oxine test for Mg, treat the acid solution with a little  $\text{NH}_4\text{Cl}$ , followed by dilute  $\text{NH}_3$  solution until basic and  $\text{Na}_2\text{HPO}_4$  solution. Shake and stir vigorously. A white crystalline ppt. of  $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$  indicates Mg. This ppt. sometimes separates slowly. Dissolve the ppt. in a little dilute HCl and apply the “magneson” test. A blue ppt. confirms Mg.

† It is advisable to test the cobalt glass with a potassium salt to be certain that the glass is satisfactory: some samples of cobalt glass completely absorb the red lines due to potassium. It is recommended that a hand spectroscope be used, if available.

‡ If the residue dissolves completely (or almost completely) in water, dilute the resulting solution (after filtration, if necessary) to about 6 ml. and divide it into three approximately equal parts:—(i) Use the major portion to test for Mg with the prepared “oxine” solution: confirm Mg by applying the “magneson” test to 3–4 drops of the solution; (ii) and (iii) Test for Na and K respectively, as described in the Table.

dry residue is extracted with water to separate the soluble Na and K salts and filtered: the residue (*R*) is tested for Mg and the filtrate (*S*) is examined for Na and K.

**Magnesium.** The residue (*R*) is dissolved in dilute HCl and the larger portion of the resulting solution is tested for Mg with the oxine reagent (Section III, 33, reaction 7): the smaller portion is subjected to the "magneson" test (Section III, 33, reaction 8) when a blue precipitate should be obtained.

The precipitation of Mg as  $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$  by the addition of a little  $\text{NH}_4\text{Cl}$  and excess of  $\text{Na}_2\text{HPO}_4$  to the ammoniacal solution (Section III, 33, reaction 5) is sometimes rather slow; also traces of Group IV metals tend to interfere. For these reasons the oxine and "magneson" tests are preferred.

**Potassium.** The precipitation of the yellow potassium cobaltinitrite with  $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$  (Section III, 34, reaction 1) and the flame test (best observed through a spectroscope) are characteristic.

**Sodium.** The most satisfactory precipitation for sodium ions is that with uranyl magnesium or zinc acetate (Section III, 35, reactions 1 and 3). The flame test, in which an intense, *persistent* yellow coloration is produced, is characteristic. Traces of sodium may be introduced from the reagents during the analysis, and hence it is important to look for a strong persistent yellow coloration; a feeble yellow coloration may be ignored.

**Ammonium** was tested for in preliminary test (v) (Section VII, 2). By heating the original substance with NaOH solution,  $\text{NH}_3$  will be evolved from ammonium salts. The  $\text{NH}_3$  gas may be identified by its odour, by its action upon red litmus paper or upon filter paper moistened with mercurous nitrate solution, or by the tannic acid-silver nitrate test (Section III, 36, reaction 7). The insertion of a *loose* plug of cotton wool in the upper part of the tube will eliminate the danger of NaOH solution spray affecting the reagent paper.

## VII, 16. EXAMINATION FOR ACID RADICALS (ANIONS) IN SOLUTION

The preliminary dry tests with dilute sulphuric acid and with concentrated sulphuric acid {Section VII, 3, tests (vi) and (vii)} will have provided useful information as to many acid radicals present. Furthermore, in the course of the examination for metal ions (cations) in solution, the presence *inter alia* of the following acid radicals will have been indicated (the first three upon treatment with hydrogen sulphide in acid solution):



*Chromate* (or *dichromate*)—reddish-yellow solution becoming green and depositing white or yellowish-white sulphur;

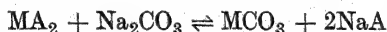
*Permanganate*—purple solution becoming nearly colourless and depositing sulphur;

*Arsenate*—yellow precipitate of arsenious sulphide slowly formed in hot solution {see Note 4 to Table I (Section VII, 6)};

*Silicate*—insoluble residue of silica after evaporating filtrate from Group II to dryness (during elimination of interfering anions prior to precipitation of Group IIIA); and

*Phosphate*—tested for with nitric acid and ammonium molybdate solution before precipitating Group IIIA.

For the examination of acid radicals or anions, it is necessary to obtain a solution containing all (or most) of the anions free, as far as possible, from heavy metals. This is best prepared by boiling the substance with concentrated sodium carbonate solution; double decomposition occurs (either partially or completely) with the production of the insoluble carbonates\* of the metals (other than alkali metals) and the soluble sodium salts of the anions, which pass into solution. Thus, if the unknown substance is the salt of a bivalent metal M and an acid HA, the following reaction will occur:



The carbonate  $MCO_3$  is insoluble and the sodium salt NaA will pass into solution whether  $MA_2$  is soluble in water or not.

**Preparation of solution for testing for anions.** Boil 1.0 gram of the finely divided substance or mixture (1) with a saturated solution of pure sodium carbonate (*ca.* 1.5*M*) (2) (prepared from 4 grams of anhydrous sodium carbonate and 25 ml. of distilled water) for 10 minutes, or until no further action appears to be taking place (3), in a small conical flask with a small funnel in the mouth to reduce the loss by evaporation; alternatively, a reflux condenser may be employed. Filter (4), wash the residue with hot distilled water and collect the washings together with the main filtrate; the total volume should be 30–35 ml. Keep the residue (5). The sodium carbonate extract will be called the “ $Na_2CO_3$  prepared solution.”

*Notes.* (1) If a solution is supplied for analysis, use sufficient to contain 1.0 gram of solid material, render it strongly alkaline with saturated sodium carbonate solution and evaporate it down to 10–15 ml.

(2) It is essential to use pure sodium carbonate; the A.R. product is satisfactory. Some “pure” samples may contain traces of sulphate

\* Certain carbonates, initially formed, are converted into insoluble basic carbonates or into hydroxides.

or chloride: the absence of these impurities should be confirmed by a blank experiment.

(3) If ammonium is present, ammonia will be evolved (indicated by the smell above the solution), continue boiling until ammonia is completely expelled, otherwise those basic elements which form ammonia complexes may pass into the sodium carbonate extract.

(4) If no precipitate is obtained, the substance is largely free from heavy metals, and the sodium carbonate treatment may be omitted if more of the solution is required. Certain amphoteric elements may, however, be present in the sodium carbonate solution, *e.g.* Cu, Sn, Sb, As, Al, Cr and Mn, dissolve in appreciable quantities; manganates, permanganates and chromates may also be present so that the colour of the solution should be noted. If cyanide is present, certain cations, such as Ag, Hg, Fe, Ni and Co, may pass into the alkaline extract by virtue of the formation of complex cyanides (anions).

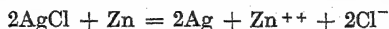
(5) The residue (R) from the  $\text{Na}_2\text{CO}_3$  treatment may contain, in addition to the carbonates, basic carbonates and hydroxides of the heavy metals, certain phosphates (*e.g.* those of Pb, Ag, Cd, Cr, Mo, Mn, Zn, Ca and Mg, which are less than 50 per cent transposed), arsenates, sulphides, fluorides, silicates and complex cyanides, and the halides of silver. This may be due in the case of products produced by high-temperature processes or of certain natural products to the slow rate of reaction with the alkali carbonate or it may be due to the fact that the solubilities are such that very little metathesis can take place. Hence the residue should be kept until the tests for anions have been completed, and then tested for the above anions if they are not found in the alkaline extract or in the preliminary tests: the original substance can, of course, be employed for these tests. After extraction of the sodium carbonate residue with dilute hydrochloric acid, the undissolved portion (R) may be treated as an insoluble substance and investigated according to Section VII, 20. It is generally more convenient, however, to test the residue (R) for the various anions as follows.

**Phosphate and arsenate.** If the " $\text{Na}_2\text{CO}_3$  prepared solution," when acidified with dilute nitric acid, boiled for 1 minute and rendered alkaline with ammonia solution, does not give a precipitate with the magnesium nitrate reagent or with magnesia mixture, phosphate and arsenate are absent. Heat a small portion of the residue with concentrated nitric acid; if brown fumes are evolved, indicating the presence of a reducing agent, add more concentrated nitric acid and continue the heating until all the reducing agent is oxidised. Dilute the solution with water, heat to boiling and filter. Render the filtrate alkaline with concentrated ammonia solution, and add the magnesium nitrate reagent or magnesia mixture. A white precipitate indicates *arsenate and/or phosphate*. Separate as described in Section IV, 45, 11 and 12.

**Sulphide.** Reduce a portion of the residue with zinc and dilute sulphuric acid. If hydrogen sulphide is evolved (lead acetate paper test), *sulphide* is present. It is preferable to employ the sodium carbonate residue (R) rather than the original mixture in testing for sulphide, for the latter may contain sulphite and thiocyanate, both of which give hydrogen sulphide with nascent hydrogen (compare Section IV, 4, reaction 8 and Section IV, 10, reaction 5).

**Cyanide.** If this is suspected, hydrogen cyanide will be evolved in the reduction with zinc and sulphuric acid, particularly on warming. Identify the hydrogen cyanide by the ammonium sulphide test (Section IV, 8, reaction 1). It will also be identified in the preliminary test with dilute sulphuric acid (Section VII, 3, test (vi)).

**Halides of silver.** Treat a portion of the residue (*R*) with zinc and dilute sulphuric acid (the solution remaining after testing for *sulphide* may be used):



Filter to remove the excess of zinc and the precipitated silver, boil the solution to remove all the hydrogen sulphide (if sulphide is present), and test the solution for  $\text{Cl}^{-}$ ,  $\text{Br}^{-}$  and  $\text{I}^{-}$  as detailed in Section IV, 45.

**Fluoride.** A portion of the dried residue (or of the original mixture) may be decomposed with concentrated sulphuric acid. Heat in a lead capsule or crucible with concentrated sulphuric acid and apply the etching test (Section IV, 17, reaction 2). Alternatively, the "water" test (Section VII, 16, reaction 8) may be used.

Use the " $\text{Na}_2\text{CO}_3$  prepared solution" to carry out the following tests.

**1. Sulphate test.** To 2 ml. of the " $\text{Na}_2\text{CO}_3$  prepared solution" add dilute hydrochloric acid until acid (test with litmus paper) and then add 1-2 ml. in excess. Boil for 1-2 minutes to expel carbon dioxide completely, and then add about 1 ml. of barium chloride solution. A white precipitate indicates *sulphate*. Confirm by the charcoal test (Section IV, 24, reaction 1).

**Silicofluorides** also give a white precipitate under the above conditions, but are of comparatively rare occurrence. They can be readily distinguished from sulphates by the action of concentrated sulphuric acid (Section IV, 27, reaction 1) and, of course, by the charcoal test.

**2. Test for reducing agents.** *Potassium permanganate test.* Acidify 2 ml. of the " $\text{Na}_2\text{CO}_3$  prepared solution" with dilute sulphuric acid and add 1 ml. of dilute sulphuric acid in excess. Add 0.5 ml. of 0.02*N* potassium permanganate solution (prepared by diluting 1 ml. of 0.1*N*  $\text{KMnO}_4$  to 5 ml.) from a dropper. Bleaching of the permanganate solution indicates the presence of one or more of the following reducing anions: *sulphite*, *thiosulphate*, *sulphide*, *nitrite*, *cyanide*, *thiocyanate*, *bromide*, *iodide*, *arsenite* and *ferrocyanide*. If the permanganate is not decolourised, heat and observe the result. If the reagent is bleached only on heating, the presence of *oxalate*, *formate* or *tartrate* is indicated. A negative test points to the absence of the above anions with the exception of cyanide, which, if present in low concentration, may not act upon the permanganate solution.

**3. Test for oxidising agents.**—*Manganous chloride reagent test.* This test depends upon the fact that a saturated solution of manganous chloride ( $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ) in concentrated hydrochloric acid is converted by even mild oxidising agents to a dark brown-coloured manganic salt, probably containing the complex  $[\text{MnCl}_6]^{--}$  or  $[\text{MnCl}_4]^-$  ions.

To 2 ml. of the " $\text{Na}_2\text{CO}_3$  prepared solution" add 1 ml. of concentrated hydrochloric acid and 2 ml. of the manganous chloride reagent. A brown (or black) coloration indicates the presence of *nitrate, nitrite, ferricyanide, chlorate, bromate, iodate, chromate* or *permanganate*. A negative test indicates the absence of the above oxidising agents except small amounts of nitrates and nitrites and of arsenate; if reducing anions have been found, this test is inconclusive.

**4. Tests with silver nitrate solution.** The separation of a comparatively large number of anions from the " $\text{Na}_2\text{CO}_3$  prepared solution" into several groups is possible with this reagent.

The presence of thiosulphate, sulphide, cyanide, sulphite, ferro- and ferri-cyanide, however, introduces difficulties in the subsequent separations, hence these anions must be tested for first and, if present, removed.

Thiosulphate will be detected in the preliminary test with dilute sulphuric acid: if it is found, it should be eliminated by heating the original mixture with dilute sulphuric acid until no more sulphur dioxide is evolved, evaporating the residual mixture just to dryness and then heating with 1.5*M* sodium carbonate solution, etc. The occurrence of thiosulphates in mixtures is comparatively rare and hence this special treatment prior to making the " $\text{Na}_2\text{CO}_3$  prepared solution" is rarely necessary. The interference of the  $\text{S}_2\text{O}_3^{--}$  ion with the silver nitrate reaction may arise from (i) the formation of a precipitate of sulphur upon acidification, (ii) the formation of white silver thiosulphate  $\text{Ag}_2\text{S}_2\text{O}_3$  which rapidly passes into the black silver sulphide  $\text{Ag}_2\text{S}$ , thus giving a false test for  $\text{S}^{--}$  ion, and (iii) under certain circumstances it will convert  $\text{CN}^-$  into  $\text{SCN}^-$  and  $\text{Fe}^{+++}$  into  $\text{Fe}^{++}$ .

**Sulphide.** This may have been detected in the preliminary test with dilute sulphuric acid. Sulphide can be readily found by adding a little lead nitrate solution to 0.5 ml. of the " $\text{Na}_2\text{CO}_3$  prepared solution," when a black precipitate of lead sulphide is produced.

**Cyanide.** This should have been detected and confirmed in the preliminary test with dilute sulphuric acid (Prussian blue test or as Section IV, 8, reaction 1).

**Sulphite.** This anion will have been detected in the preliminary test with dilute sulphuric acid (potassium dichromate paper or fuchsin solution test).

**Ferrocyanide (and Thiocyanate).** Acidify 1 ml. of the " $\text{Na}_2\text{CO}_3$  prepared solution" with dilute hydrochloric acid and add a few drops of ferric chloride solution. A deep blue precipitate indicates *ferrocyanide present*. Now add 0.5–1 ml. of ferric chloride solution, 0.2 gram of sodium chloride and half a Whatman filtration accelerator, shake the mixture vigorously and filter. A deep red filtrate indicates *thiocyanate present*.

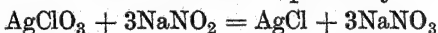
**Ferricyanide.** Acidify 1 ml. of the " $\text{Na}_2\text{CO}_3$  prepared solution" with dilute hydrochloric acid and add a few drops of freshly prepared ferrous sulphate solution. A deep blue precipitate indicates *ferricyanide present*. This precipitate should not be confused with that of light grey-blue colour produced by a ferrocyanide.

Use is made of the following facts in the preliminary and partial separation of anions with silver nitrate solution:

(1) In dilute nitric acid solution (*ca.* 1.5*N*), chloride, bromide, iodide, iodate and thiocyanate are precipitated.

It will be appreciated that iodate is incompatible with both iodide (compare Section IV, 21, reaction 6) and with thiocyanate (Section IV, 21, reaction 9) since iodine is liberated in acid solution. Also sulphide is incompatible with both bromate and iodate (oxidation to sulphate occurs), and an arsenite is oxidised by iodate in acid solution. These facts should therefore be borne in mind when interpreting Table XI. An independent test for iodate (test 11) is provided below: this can be performed before the silver nitrate tests.

(2) Upon treatment of the filtrate from (1) with sodium nitrite solution, chlorate and bromate are reduced to the simple halides, the presence of which is revealed by the separation of silver chloride and silver bromide respectively.



Chromates (which, of course, yield a coloured solution) are simultaneously reduced to chromic salts.

(3) If the acidity of the filtrate from (2) is reduced (to about pH 5) by just neutralising with sodium hydroxide solution and adding dilute acetic acid, silver nitrate solution will precipitate phosphate, arsenate, arsenite,\* oxalate and possibly other organic acids.

It cannot be too strongly emphasised that Table XI is intended to act merely as a guide and to indicate the presence of groups of anions; it should therefore be considered carefully in conjunction with the various observations which have been made in the preliminary tests and particular note be taken of

\* It must be remembered that arsenite may be partially oxidised by the dilute nitric acid treatment and also by other oxidising anions which may be present. Arsenite is, however, readily detected in the analysis for cations (compare Section III, 11, reaction 1).

possible interferences. The Table should therefore not be interpreted as rigidly as a Group Separation Table for cations.

**Table XI.—Separation of Anions with Silver Nitrate Solution**

<p>It is essential to remove interfering anions first in the following order. These anions, if present, will have been detected in the preliminary tests.</p> <p><b>1. Sulphide, cyanide and sulphite.</b> Acidify 10 ml. of the "<math>\text{Na}_2\text{CO}_3</math> prepared solution" with dilute acetic acid and boil gently for 3–4 minutes: make certain that the solution remains acid (e.g. to litmus) throughout. If sulphite is present, it is advisable to heat the solution for 10–15 minutes (maintaining the volume, if necessary) whilst a stream of air is drawn through it (compare Fig. IV, 45, 1): test for complete removal of sulphur dioxide with fuchsin solution.</p> <p><b>2. Ferrocyanide and ferricyanide.</b> Employ the original solution from 1 or, if sulphide, cyanide and sulphite are absent, use 10 ml. of the "<math>\text{Na}_2\text{CO}_3</math> prepared solution" made acid (to Congo red) with dilute acetic acid. Add 0.5M zinc nitrate solution until precipitation ceases, introduce a Whatman filtration accelerator, stir and filter the zinc ferro- and ferricyanides in the cold; wash with a little 0.1M zinc nitrate solution.</p>			
<p>Use the filtrate from 2 or, if ferrocyanide and/or ferricyanide and other interfering anions are absent, acidify 10 ml. of the "<math>\text{Na}_2\text{CO}_3</math> prepared solution" cautiously with dilute <math>\text{HNO}_3</math> (to litmus or other indicator paper). Add one-tenth of the volume of concentrated <math>\text{HNO}_3</math>, stir for 30 seconds and then add <math>\text{AgNO}_3</math> solution with stirring until precipitation is complete. Heat to the boiling point, allow the ppt. to settle, cool and filter. Wash the ppt. with 2–3 ml. of N nitric acid.</p>			
<p><b>Residue (A).</b> Yellow or white. May contain: <math>\text{AgCl}</math>, <math>\text{AgBr}</math>, <math>\text{AgI}</math> (or <math>\text{AgIO}_3</math>), <math>\text{AgSCN}</math>. Use Table A.</p>	<p><b>Filtrate.</b> Add 1 ml. of <math>\text{AgNO}_3</math> solution, then 20% <math>\text{NaNO}_2</math> solution (prepared from the A.R. solid) dropwise and with stirring until precipitation is complete. [If no ppt. forms, do not add more than 0.5 ml. of <math>\text{NaNO}_2</math> solution.] Filter, and wash with 2–3 ml. of N nitric acid.</p>		
	<p><b>Residue (B).</b> May contain <math>\text{AgCl}</math> and <math>\text{AgBr}</math> derived from <math>\text{AgClO}_3</math> and <math>\text{AgBrO}_3</math>. Use Table B.</p>	<p><b>Filtrate.</b> Add <math>\text{NaOH}</math> solution (use a dropper) with vigorous stirring until neutral to litmus (1), then 0.5 ml. of dilute acetic acid, followed by 1 ml. of <math>\text{AgNO}_3</math> solution. Heat the mixture to about <math>80^\circ\text{C}</math> (2). If a permanent precipitate forms, add more <math>\text{AgNO}_3</math> solution until precipitation is complete. Filter and wash with hot water.</p>	
		<p><b>Residue (C) (3).</b> <math>\text{Ag}_3\text{PO}_4</math>—yellow. <math>\text{Ag}_3\text{AsO}_4</math>—brownish-red. <math>\text{Ag}_3\text{AsO}_3</math>—yellow. <math>\text{Ag}_2\text{C}_2\text{O}_4</math>—white (4). Use Table C.</p>	<p><b>Filtrate.</b> Discard.</p>

**Notes.** (1) The sodium hydroxide solution should be added until the first permanent precipitate of C or of brown silver oxide appears. The solution must not be allowed to become alkaline to litmus for this will produce a large precipitate of silver oxide which redissolves only slowly.

The pH required for the precipitation of *C* is about 5.5; this can be more conveniently achieved by the use of either nitrazine (sodium dinitrophenyl-azo-naphthol sulphonate) or bromocresol purple (di-bromo-*o*-cresol-sulphone-phthalein) test-papers. All that is necessary is to add the sodium hydroxide solution until the appropriate colour change is produced; it is best to use a standard for comparison (nitrazine, pH range 5.5–7.2, yellow to blue; bromocresol purple, pH range 5.2–6.8, yellow to purple).

(2) A crystalline precipitate of silver acetate may separate here; this dissolves when the solution is heated.

(3) Chromate, if present, would normally be precipitated at a pH of about 5.5, but the sodium nitrite treatment in *B* reduces it to the chromic state. Chromic hydroxide is not precipitated in the acetic acid-acetate solution unless present in very large amounts.

(4) Other organic acids may also separate here. If only a white precipitate is obtained, use the organic acids separation table of Section IV, 45, 20. The presence of organic acids will also be indicated by some of the preliminary tests.

#### Table A (*Examination of Residue A*)

**Thiocyanate test.** Test one-quarter of the precipitate *A* for thiocyanate by heating for 3–4 minutes with 5 ml. of 5 per cent NaCl solution (this converts part of the AgSCN into NaSCN), cool and allow the precipitate to settle. Treat the supernatant liquid with 1 ml. of dilute HCl and a few drops of FeCl<sub>3</sub> solution. Red coloration. *Thiocyanate present.*

If thiocyanate is present, it must be destroyed since it interferes with the tests for the halides. Heat the remainder of the residue *A* (previously dried in the steam oven or in an air bath) in a porcelain crucible, gently at first and then gradually to dull redness until all the thiocyanate is decomposed, *i.e.* until blackening of the precipitate and/or burning of *S* ceases.

To the residue in the crucible (if thiocyanate is present) or to the remainder of the residue *A* transferred to a small beaker (if thiocyanate is absent), add 1–2 grams of granulated zinc (but preferably of 20 mesh) and 5–10 ml. of dilute H<sub>2</sub>SO<sub>4</sub>. Allow the reduction to proceed for 10 minutes with frequent stirring; gentle warming may be necessary to start the reaction. Filter and wash the precipitate with a little dilute H<sub>2</sub>SO<sub>4</sub>. Divide the filtrate into three equal parts.\*

\* The preliminary test with concentrated H<sub>2</sub>SO<sub>4</sub> will generally indicate the presence of any of the three halides or mixtures of them. For individual halides, the confirmatory tests of Section VII, 17, may be used. If mixtures are present, the methods described in Section IV, 45, 5–8, may be adopted. For those who prefer systematic testing for any or all of the halides, the alternative procedures in Table A are recommended.

**Iodide test.** Add 1–2 ml. of  $\text{CCl}_4$  and 3 ml. of 10-volume  $\text{H}_2\text{O}_2$  or 3 ml. of 25 per cent  $\text{Fe}_2(\text{SO}_4)_3$  solution to one-third of the filtrate. Shake vigorously and allow to settle. Purple to violet coloration of  $\text{CCl}_4$  layer. *Iodide present.*

**Bromide test.** (a) If iodide is present, this must be removed by treating one-third of the solution with 5 ml. of dilute  $\text{H}_2\text{SO}_4$  and 2 ml. of 30 per cent  $\text{NaNO}_2$  solution (chloride-free). Boil the solution with stirring, concentrate to 3 ml. and allow to cool. Test for bromide as under (b).

(b) If iodide is absent, use one-third of the solution directly. Add an equal volume of concentrated  $\text{HNO}_3$ , immerse the test-tube in a beaker of boiling water for 1 minute and cool to room temperature with cold water. Add 1–2 ml. of  $\text{CCl}_4$  and stir vigorously with a glass rod (if a glass-stoppered tube or conical flask is available, this will facilitate shaking). Yellow or brown colour of the  $\text{CCl}_4$  layer. *Bromide present.*

**Chloride test.** (a) If iodide and/or bromide present, dilute the remaining third of the solution to 15 ml., add 8 ml. of concentrated  $\text{HNO}_3$  and boil (glass rod in beaker) for 5 minutes or until no more  $\text{Br}_2$  is given off. Cool and test for chloride as in (b) below with  $\text{AgNO}_3$  solution only.

(b) If bromide and iodide are absent, add 3–4 ml. of dilute  $\text{HNO}_3$  and 3 ml. of  $\text{AgNO}_3$  solution; stir and heat to boiling. White precipitate. *Chloride present.*

### Table B (*Examination of Residue B*)

Suspend the residue *B* in 5–10 ml. of dilute sulphuric acid in a beaker, and add 1–2 grams of granulated zinc (but preferably of 20 mesh). Allow the reduction to proceed for 10 minutes with frequent stirring; gentle warming may be necessary to start the reaction. Filter and wash the precipitate with a little dilute sulphuric acid. Examine the solution for chloride and bromide as in Table A.

### Table C (*Examination of Residue C*)

If the precipitate is white, only organic acids may be present and the other anions need not be tested for. Furthermore, the preliminary tests of heating alone and heating with concentrated sulphuric acid will have indicated the presence of organic acids. If organic acids are indicated or suspected, use the separation Table given in Section IV, 45, 20.

If the precipitate is yellow phosphate and/or arsenite may be present and arsenate is absent. The following scheme provides for the separation of phosphate, arsenate and arsenite.



Dissolve the residue *C* (1), which may contain  $\text{Ag}_3\text{PO}_4$ ,  $\text{Ag}_3\text{AsO}_4$  and  $\text{Ag}_3\text{AsO}_3$ , by pouring 10–15 ml. of 3*N* HCl repeatedly through it. Filter and wash with 5 ml. of 0.1*N* HCl.

**Residue.**  
AgCl.  
Reject.

**Filtrate.** Render alkaline with dilute aqueous  $\text{NH}_3$  and add 5 ml. in excess (2). Add 10 ml. of the  $\text{Mg}(\text{NO}_3)_2$  reagent, allow to stand for 10 minutes, stirring frequently, and filter. Wash the ppt. with 5 ml. of 0.1*N*  $\text{NH}_3$  solution.

**Residue.** May contain  $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{Mg}(\text{NH}_4)\text{AsO}_4 \cdot 6\text{H}_2\text{O}$  (3). Dissolve the ppt. by pouring 10 ml. of dilute HCl repeatedly through the filter. Add to the cold solution 0.5 gram of solid  $\text{NaHCO}_3$  and 0.5 gram of solid KI. An immediate yellow to brown iodine colour indicates arsenate. Saturate the solution with  $\text{H}_2\text{S}$  (under “pressure”). Filter and wash with 0.5*N* HCl.

**Filtrate.** Add 4 ml. of 3%  $\text{H}_2\text{O}_2$  solution, heat nearly to boiling (to oxidise arsenite to arsenate), cool and allow to stand for 10 minutes; shake frequently. Filter.

**Residue.**  
 $\text{Mg}(\text{NH}_4)\text{AsO}_4 \cdot 6\text{H}_2\text{O}$ .  
Arsenite present.

**Filtrate.**  
Reject.

**Residue.**  
Yellow:  
 $\text{As}_2\text{S}_3$ .  
Arsenate present.

**Filtrate.** Boil until  $\text{H}_2\text{S}$  is expelled and the volume is ca. 10 ml. Filter and discard any ppt. of S. Render alkaline with concentrated  $\text{NH}_3$  solution and add 3 ml. in excess. Add 5 ml. of the  $\text{Mg}(\text{NO}_3)_2$  reagent and allow to stand, with frequent stirring, for 10 minutes.

White ppt. of  
 $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$ .  
Phosphate present.

**Notes.** (1) The “ $\text{Na}_2\text{CO}_3$  prepared solution” may also be used for the detection of arsenate, phosphate and arsenite. Acidify 10 ml. of the “ $\text{Na}_2\text{CO}_3$  prepared solution” with dilute HCl and then render alkaline with dilute aqueous  $\text{NH}_3$ . Filter, if necessary, and reject any precipitate. Treat the clear solution with the  $\text{Mg}(\text{NO}_3)_2$  reagent, etc., and proceed as in Table.

(2) If chromate is present, it will have been reduced to chromic ion by the  $\text{NaNO}_2$  solution and may be partly precipitated as  $\text{Cr}(\text{OH})_3$ . This will be dissolved by HCl and reprecipitated by the aqueous  $\text{NH}_3$ . Hence any precipitate formed at this point should be filtered off before the  $\text{Mg}(\text{NO}_3)_2$  reagent is added.

(3) If phosphate has been detected previously (*e.g.* in the cation analysis), a qualitative test for arsenate may be made as follows. Pour 1 ml. of  $\text{AgNO}_3$  solution, to which 2 drops of dilute acetic acid have been added, over the white precipitate. A brownish-red coloration of the precipitate confirms the presence of *arsenate*. The acetic acid is added to increase the solubility of the magnesium salt and thus facilitate the conversion of magnesium ammonium arsenate to the characteristic silver arsenate.

**5. Test with calcium chloride solution.** For tests 5–7 a “ $\text{Na}_2\text{CO}_3$  practically neutral solution” is required. This is prepared as follows. Take 10 ml. of “ $\text{Na}_2\text{CO}_3$  prepared solution” in a porcelain dish and render it faintly acid with dilute nitric acid (use litmus paper or other equivalent test-paper). Boil for 1–2 minutes to expel carbon dioxide, allow to cool, then add dilute ammonia solution until just alkaline\* and boil for 1 minute to expel the slight excess of ammonia. Divide the solution into three equal parts for tests 5, 6 and 7.

Add  $\text{CaCl}_2$  solution (equal in volume to that of the solution) and allow to stand for several minutes. A white precipitate indicates *fluoride, oxalate, phosphate, arsenate and tartrate*†; a precipitate which separates on boiling for 1–2 minutes is *citrate*. Of these only oxalate and fluoride are insoluble in dilute acetic acid. Hence extract the white precipitate with dilute acetic acid and filter. A residue (*R*) insoluble in dilute acetic acid, indicates *oxalate and/or fluoride*. Exactly neutralise the acetic acid solution by adding sodium hydroxide solution from a dropper and testing with an indicator paper or solution (bromothymol blue or nitrazine yellow is suitable); a white precipitate indicates the presence of phosphate, arsenate and/or tartrate. The precipitate often separates slowly. Add a little silver nitrate solution to the suspension or solution: a yellow precipitate indicates the presence of phosphate; a brownish-red precipitate indicates arsenate or arsenate plus phosphate.

It is convenient to test the residue *R* for oxalate here. Dissolve it by pouring hot dilute sulphuric acid into the filter. Treat the hot filtrate with a few drops of 0.02*N* potassium permanganate solution. If the permanganate solution is reduced, *oxalate is present*. If no reduction occurs, the presence of fluoride is indicated.

\* If a precipitate forms on neutralising the solution, the presence of arsenic, antimony and tin sulphides and possibly salts of amphoteric elements (lead, tin, aluminium and zinc) is indicated. The precipitate should be filtered off and rejected.

†  $\text{CaSO}_4$  and  $\text{Ca}(\text{BO}_2)_2$  may separate from sufficiently concentrated solutions.

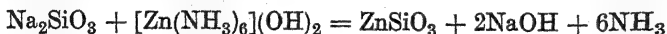
6. **Test with ferric chloride solution.** Treat the second third of the " $\text{Na}_2\text{CO}_3$  practically neutral solution" drop by drop with ferric chloride solution until no further change occurs.

(The bench reagent contains free hydrochloric acid; add dilute ammonia solution until a precipitate just forms, filter and use the filtrate for the test. The filtrate is sometimes termed "neutral  $\text{FeCl}_3$  solution".)

Yellow to brown precipitate.	<i>Benzoate, succinate (also chromate, phosphate, arsenate and borate, all of which have been or will be found by other tests).</i>
Blue precipitate.	<i>Ferrocyanide.</i>
Reddish-brown coloration, ppt. after dilution and boiling.	<i>Acetate, formate.</i>
Blood-red coloration discharged by $\text{HgCl}_2$ solution.	<i>Thiocyanate (sulphocyanide).</i>
Reddish-purple coloration; colour vanishes on warming.	<i>Thiosulphate.*</i>
Brown coloration; blue ppt. with $\text{FeSO}_4$ solution.	<i>Ferricyanide.</i>
Violet coloration.	<i>Salicylate.</i>
Greenish-black coloration.	<i>Gallate.</i>
Bluish-black coloration.	<i>Tannate.</i>

7. **Test for silicate.** To the remaining third of the " $\text{Na}_2\text{CO}_3$  practically neutral solution" add ammonium chloride and ammonium carbonate solution. A gelatinous precipitate indicates *silicate*.

A more satisfactory reagent for the precipitation of silicates is hexammine zinc hydroxide,  $[\text{Zn}(\text{NH}_3)_6](\text{OH})_2$ . This precipitates zinc silicate  $\text{ZnSiO}_3$ , which is much more difficultly soluble in dilute alkaline solution than is the free silicic acid.



The reagent is added in slight excess and the solution boiled until all the ammonia is expelled.

The reagent is prepared by treating pure zinc nitrate solution with potassium hydroxide solution, filtering off the precipitated zinc hydroxide, washing well, and dissolving the precipitate in dilute ammonia solution.

\* As a general rule, thiosulphate will not be found here as it should have been more or less completely decomposed in the preparation of the " $\text{Na}_2\text{CO}_3$  practically neutral solution."

**8. Test for fluoride.** The presence of fluoride will have been indicated in the preliminary test with concentrated sulphuric acid by the "oily" or "greasy" appearance of the tube and also by the calcium chloride solution test. It may be confirmed by the following test.

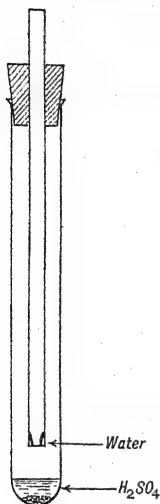
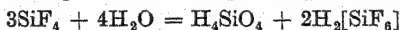
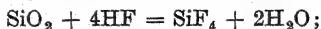


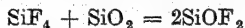
Fig. VII, 16, 1

Fit a small test-tube with a cork carrying a piece of glass tubing open at both ends; cut a V-shaped groove in the side of the cork to allow for the expansion of the air in the tube when heated. Mix a small quantity of the original substance in a crucible with about three times its bulk of ignited silica (quartz powder is preferable, but results are obtained with precipitated silica), transfer it carefully to the tube, and add by means of a dropper or small pipette about twice as much (by volume) of concentrated sulphuric acid as there is solid. Introduce the glass tube, wet on the inside with water thus forming a ring of water at the lower end (Fig. VII, 16, 1), into the test-tube and adjust its height so that the bottom is at a distance of approximately one and a half times the diameter of the tube from the paste in the test-tube. Heat the mixture *gently* over a small flame for 2-3 minutes. A white film of silicic acid in the water confirms the presence of *fluoride*.

The reactions which occur are:



When the highly reactive precipitated silica is employed, much of the  $\text{SiF}_4$  reacts with it to form a stable oxyfluoride, probably



Hence the relatively unreactive powdered quartz is to be preferred.

**9. Test for cyanide.** This is sometimes missed in the preliminary test with dilute sulphuric acid and in the potassium permanganate test for reducing anions. The following test is conclusive. Use the apparatus described in the test for carbonates (Fig. IV, 2, 1). Place 0.2 gram of the substance in the test-tube together with three or four fragments of marble. Introduce 5 ml. of 2-3 *N* hydrochloric acid, replace the cork immediately and allow the evolved gas to bubble through

5 ml. of 2-3 *N* sodium hydroxide solution. After 5-10 minutes add 0.5 ml. of saturated ferrous sulphate solution to the alkaline solution, heat to the boiling point, cool thoroughly, acidify with concentrated hydrochloric acid and add a few drops of ferric chloride solution. A blue precipitate (Prussian blue) is obtained; with small amounts of cyanide the solution acquires a blue or blue-green colour.

The test may also be conducted with the 2 ml. of the " $\text{Na}_2\text{CO}_3$  prepared solution." Carbonate, sulphite and thiosulphate have no influence upon the reaction. Nitrite interferes, presumably owing to the oxidation of the hydrogen cyanide. In the presence of sulphide, the test is complicated by the precipitation of black ferrous sulphide when ferrous sulphate is added to the alkaline solution. It is best to boil the solution containing the suspended ferrous sulphide, acidify with hydrochloric acid and boil again to expel most of the dissolved hydrogen sulphide; upon adding a drop of ferric chloride solution, a blue precipitate is produced if cyanide is present.

Complex cyanides, such as ferrocyanide and ferricyanide, do not interfere when the test is conducted in the cold.

**10. Test for chromate.** If the " $\text{Na}_2\text{CO}_3$  prepared solution" is colourless, chromate is absent. If yellow, chromate may be present; ferro- and ferri-cyanides also impart a yellow colour to the solution. The presence of chromate will have been indicated by the precipitation of green chromic hydroxide in the silver nitrate solution tests (*Table C*) and also in the analysis for cations.

To confirm chromate, acidify 2 ml. of the " $\text{Na}_2\text{CO}_3$  prepared solution" with dilute sulphuric acid, boil for one minute to expel  $\text{CO}_2$ , etc., filter if necessary, add 1-2 ml. of amyl alcohol, followed by 1-2 ml. 10-volume hydrogen peroxide and shake gently (compare Section IV, 33, reaction 4). A blue coloration of the amyl alcohol layer confirms *chromate*.

**11. Test for iodate.** This anion will give a positive test for oxidising agents, but will not normally be detected in the systematic analysis.

The presence of iodate in the " $\text{Na}_2\text{CO}_3$  prepared solution" can be readily detected as follows. Treat 2 ml. of the solution with silver nitrate solution until precipitation ceases, heat to boiling for 2-3 minutes and filter. Render the filtrate strongly acid with hydrochloric acid, add 2 ml. of 10 per cent ferrous sulphate solution (or 10 per cent sodium bisulphite solution) and shake it with 2 ml. of carbon tetrachloride. A purple coloration of the organic layer indicates *iodate*.

This test utilises the fact that silver iodide, but not silver

iodate, is precipitated upon the addition of silver nitrate to the " $\text{Na}_2\text{CO}_3$  prepared solution."

An iodate does not react with concentrated sulphuric acid in the cold or upon gentle heating. A solution of an iodate gives with silver nitrate solution a white precipitate of silver iodate, insoluble in *N* nitric acid but soluble in dilute ammonia solution, thus simulating the behaviour of a chloride towards these reagents. Iodates, however, give a white precipitate of barium iodate  $\text{Ba}(\text{IO}_3)_2$  with barium chloride solution; the precipitate is sparingly soluble in dilute nitric acid.

**12. Test for periodate (1).** This anion will give a positive test for oxidising agents, but will not be detected in the systematic analysis. It will be necessary to remove first iodide or iodate by precipitation with silver nitrate in acid solution, and the excess of silver ions with sodium chloride solution: the resulting solution is strongly acidified with hydrochloric acid and a ferrous salt is added. If a periodate is present, it will be reduced to iodine, which can be identified with carbon tetrachloride.

Acidify 3 ml. of the " $\text{Na}_2\text{CO}_3$  prepared solution" with 60 per cent perchloric acid and add 1 ml. in excess (2); add silver nitrate solution, slowly and with stirring, until precipitation is complete. Filter and collect the filtrate in a ground-glass stoppered conical flask or test-tube. Add 5 per cent sodium chloride solution, 0.5 ml. at a time, to the filtrate until no more precipitate forms. Stopper the flask or test-tube and shake the mixture vigorously after each addition. Filter off the silver chloride (3), transfer the filtrate to the stoppered vessel, add an equal volume of concentrated hydrochloric acid (if a precipitate of sodium chloride forms, filter), cool, then add 1–2 grams of solid ferrous ammonium sulphate and 2 ml. of carbon tetrachloride. Shake the mixture intermittently for 5 minutes. A purple colour in the carbon tetrachloride indicates *periodate present*.

**Notes.** (1) This anion is rarely encountered and need not be tested for in general qualitative analysis. It is given here for the sake of completeness as no reactions for periodates are included in Chapter IV. Four tests which **distinguish periodates from iodates** are:

- (a) With mercuric nitrate solution an orange-red precipitate of  $\text{I}_2\text{O}_5 \cdot 5\text{HgO}$  is obtained {compare iodates which give white  $\text{Hg}(\text{IO}_3)_2$ }.
- (b) Upon boiling with 10 per cent nitric acid and a little manganous sulphate solution, a purple solution of permanganic acid is produced (compare iodates, which do not yield permanganic acid).

- (c) With silver nitrate solution a chocolate-brown precipitate ( $\text{Ag}_5\text{IO}_6$ ) is obtained; this darkens on boiling and is soluble in dilute nitric acid (compare silver iodate  $\text{AgIO}_3$ , which is white and sparingly soluble in dilute nitric acid).
- (d) With barium chloride solution a white precipitate is produced, which is soluble in dilute nitric acid (compare barium iodate, which is sparingly soluble in dilute nitric acid).

(2) Nitric acid tends to oxidise ferrous iron, hence it is advisable to maintain the nitrate ion concentration as low as possible and to keep the solution cold.

(3) The excess of silver ions is removed as silver chloride because they are reduced by ferrous salts to silver.

The preliminary dry tests and the reactions in solution described above will give a general (and, in some cases, a particular) indication of the nature of the acid radicals or anions present. For a number of anions (*e.g.* thiocyanate, chloride, bromide, iodide, iodate, bromate, chlorate, phosphate, silicate, fluoride, cyanide and chromate), the tests are more or less conclusive. However, in the presence of mixtures of anions, it will be necessary to distinguish between those which give analogous reactions, for example, (i) sulphite, thiosulphate and sulphate; (ii) chloride, chlorate and perchlorate; (iii) arsenite, arsenate and phosphate; (iv) ferricyanide and ferrocyanide; (v) acetate and formate; (vi) succinate and benzoate; and (vii) oxalate, tartrate and citrate. In some cases one anion interferes with the reaction of the other, *e.g.* (viii) carbonate and sulphite; (ix) nitrite and nitrate; (x) nitrate in the presence of bromide, iodide, chlorate and perchlorate; (xi) iodate and iodide; (xii) oxalate and fluoride; and (xiii) chloride and cyanide. This subject is fully discussed in Section IV, 45. Particular attention is directed to the table of separation of organic acids (IV, 45, 20): this must be used with due consideration as to the influence of interfering organic acids (compare tests 5 and 6 above).

## VII, 17. CONFIRMATORY TESTS FOR ACID RADICALS OR ANIONS

In every case where the presence of any acid radical has been indicated, it must be confirmed by at least one distinctive confirmatory test. Conclusive tests for anions (halides, sulphate, oxy-halides, thiocyanate, phosphate, silicate, fluoride, cyanide and chromate) have already been given in Section VII, 16, it will, of course, be unnecessary to confirm these further. The following list, which, for the sake of completeness includes those anions already referred to, will assist the student in the

choice of suitable tests. Full experimental details will be found in Chapter IV under the reactions of the acid radicals (anions); the reference to these will be abbreviated as follows: thus (IV, 2, 7) is to be interpreted as Section IV, 2, reaction 7. It is assumed, of course, that interfering acids are absent or have been removed.

**Chloride.** (i) Heat solid with concentrated  $\text{H}_2\text{SO}_4$  and  $\text{MnO}_2$ ;  $\text{Cl}_2$  evolved (bleaches litmus paper and also turns KI-starch paper blue) (IV, 14, 2). (ii) Chromyl chloride test (IV, 14, 5). (iii) Silver chloride-sodium arsenite test (IV, 14, 3).

**Bromide.** (i) Heat solid with concentrated  $\text{H}_2\text{SO}_4$  and  $\text{MnO}_2$ ;  $\text{Br}_2$  evolved (IV, 15, 2). (ii)  $\text{NaOCl-HCl}$  and  $\text{CHCl}_3$  or  $\text{CCl}_4$  test; yellowish-brown to yellow coloration (IV, 15, 5).

**Iodide.** (i)  $\text{NaOCl-HCl}$  (or chlorine water) and  $\text{CHCl}_3$  or  $\text{CCl}_4$  test; violet coloration (IV, 16, 4). (ii)  $\text{NaOCl-HCl}$  and starch paste test; blue coloration (IV, 16, 4).

**Fluoride.** (i) Etching test (IV, 17, 2). (ii) Silicon tetrafluoride test {heat with concentrated sulphuric acid in a test-tube} (IV, 17, 1); better, test 8 in VII, 16. (iii) Zirconium-alizarin test (IV, 17, 6).

**Cyanide.** (i) Prussian blue test (IV, 8, 4); better, test 9 in VII, 16. (ii) Ammonium sulphide test (IV, 8, 1, 6).

**Nitrite.** (i) Brown ring test with dilute acetic acid or with dilute sulphuric acid (IV, 7, 2). (ii) Thiourea test (IV, 7, 9). (iii) Sulphanilic acid- $\alpha$ -naphthylamine reagent test (IV, 7, 10).

**Nitrate.** (i) Brown ring test with concentrated  $\text{H}_2\text{SO}_4$  (IV, 18, 3), if bromide, iodide and nitrite absent. (ii) Ammonia test with Devarda's alloy (IV, 18, 4).

**Sulphide.** (i) Dilute  $\text{H}_2\text{SO}_4$  on solid, and action of  $\text{H}_2\text{S}$  on lead or cadmium acetate paper (IV, 6, 1). (ii) Sodium nitroprusside test (IV, 6, 6).

**Sulphite.** (i) Dilute  $\text{H}_2\text{SO}_4$  on solid, and action of  $\text{SO}_2$  upon potassium dichromate paper (IV, 4, 1). (ii)  $\text{BaCl}_2\text{-Br}_2$  water test (IV, 4, 2). (iii) Fuchsin solution test (IV, 4, 10).

**Thiosulphate.** (i) Action of dilute  $\text{H}_2\text{SO}_4$  upon solid, and liberation of  $\text{SO}_2$  (dichromate paper test or fuchsin solution test) and sulphur (IV, 5, 1). (ii) Potassium cyanide test (IV, 5, 6). (iii) Nickel ethylenediamine test (IV, 5, 9).

**Sulphate.** (i)  $\text{BaCl}_2$  solution and dilute  $\text{HCl}$  test, and reduction to sulphide {test for latter with sodium nitroprusside or lead acetate solution} (IV, 24, 1). (ii) Lead acetate test and solubility of  $\text{PbSO}_4$  in ammonium acetate solution (IV, 24, 2).

**Carbonate.** (i) Action of dilute  $\text{H}_2\text{SO}_4$  upon solid, and lime water or baryta water test (IV, 2, 1).



**Hypochlorite.** (i) Action of dilute HCl, and test for  $\text{Cl}_2$  evolved (IV, 13, 1). (ii) Cobalt nitrate solution test (IV, 13, 4).

**Chlorate.** (i) Sodium nitrite test (IV, 19, 4; also test 4 in VII, 16). (ii) Ferrous sulphate test (IV, 19, 6).

**Bromate.** (i) Action of concentrated  $\text{H}_2\text{SO}_4$ ;  $\text{Br}_2$  and  $\text{O}_2$  evolved (IV, 20, 1). (ii) Hydrobromic acid test (IV, 20, 4).

**Iodate.** (i) Potassium iodide test (IV, 21, 6). (ii) Sulphur dioxide or hydrogen sulphide test (IV, 21, 5).

**Perchlorate.** (i) Action of heat and test for chloride (IV, 22, 7), and non-reduction with  $\text{NaNO}_2$  or  $\text{FeSO}_4$  in acid solution (IV, 22, 5).

**Borate.** (i) Flame test (IV, 23, 2; better, test (ix) in Section VII, 3). (ii) Turmeric paper test (IV, 23, 3).

**Silicate.** (i) Microcosmic bead test (IV, 26, 5) and silicon tetrachloride test (IV, 26, 6). (ii) Ammonium molybdate solution and  $\text{SnCl}_2$  solution test (IV, 26, 8).

**Silicofluoride.** (i) Action of concentrated  $\text{H}_2\text{SO}_4$  and  $\text{BaCl}_2$  solution test (IV, 27, 1, 2).

**Persulphate.** (i) Action of boiling water (IV, 25, 1). (ii) Manganous sulphate solution test (IV, 25, 5).

**Chromate.** (i) Hydrogen peroxide test (IV, 33, 4). (ii) Lead acetate solution test (IV, 33, 3). (iii) Action of hydrogen sulphide or sulphur dioxide (IV, 35, 5, 6). (iv) Solid when warmed with a solid chloride and concentrated  $\text{H}_2\text{SO}_4$  evolves chromyl chloride (IV, 14, 5). (v) Diphenylcarbazide reagent test (IV, 33, 10).

**Permanganate.** (i) Hydrogen peroxide test, and identification of  $\text{Mn}^{++}$  ion (IV, 34, 1). (ii) Action of oxalic acid, and identification of  $\text{Mn}^{++}$  ion (IV, 37, 4). (iii) Action of hydrogen sulphide or sulphur dioxide (IV, 34, 2).

**Arsenite.** (i) Action of  $\text{H}_2\text{S}$  upon acid solution (III, 11, 1). (ii) Silver nitrate solution test (III, 11, 2), and absence of precipitate with magnesium nitrate reagent (III, 11, 3) or on boiling with ammonium molybdate solution and nitric acid. (iii) Bettendorff's test (III, 11, 6).

**Arsenate.** (i) Action of  $\text{H}_2\text{S}$  on acid solution (III, 12, 1), and silver nitrate solution test upon practically neutral solution (III, 12, 2). (ii) Magnesium nitrate reagent test (III, 12, 3). (iii) Ammonium molybdate test (III, 12, 4).

**Orthophosphate.** (i) Ammonium molybdate test (temperature not above  $40^\circ$ ) (IV, 28, 4). (ii) Magnesium nitrate reagent test (IV, 28, 3).

**Phosphite.** (i) Silver nitrate solution test (IV, 30, 1), and  $\text{Zn} +$  dilute  $\text{H}_2\text{SO}_4$  test (IV, 30, 6).

**Hypophosphite.** (i) Silver nitrate solution test (IV, 31, 1), copper sulphate solution test (IV, 31, 4), and ammonium molybdate test (IV, 31, 9).

**Cyanate.** (i) Dilute  $\text{H}_2\text{SO}_4$  test (IV, 9, 1). (ii) Cobalt acetate solution test (IV, 9, 5). (iii) Copper sulphate-pyridine test (IV, 9, 6).

**Ferrocyanide.** (i) Ferric chloride solution test (IV, 11, 3). (ii) Ferrous sulphate solution test (IV, 11, 4). (iii) Uranyl acetate solution test (IV, 11, 11). (iv) Titanium tetrachloride test (IV, 11, 9).

**Ferricyanide.** (i) Ferrous sulphate solution test (IV, 12, 3). (ii) Ferric chloride solution test (IV, 12, 4).

**Thiocyanate.** (i) Ferric chloride solution test; colour discharged by  $\text{HgCl}_2$  solution or by  $\text{NaF}$  solution, but not by dilute  $\text{HCl}$  (IV, 10, 6). (ii) Cobalt nitrate solution test (IV, 10, 7). (iii) Copper sulphate-pyridine test (IV, 10, 9).

**Acetate.** (i) Action of ethyl or of *iso*-amyl alcohol and concentrated  $\text{H}_2\text{SO}_4$  (IV, 35, 3),  $\text{AgNO}_3$  solution test (IV, 35, 4) and  $\text{FeCl}_3$  solution test (IV, 35, 6). (ii) Cacodyl oxide test (IV, 35, 7). (iii) Indigo test (IV, 35, 9).

**Formate.** (i) Mercuric chloride solution test (IV, 36, 7) or  $\text{AgNO}_3$  solution test (IV, 36, 4), and  $\text{FeCl}_3$  solution test (IV, 36, 6). (ii) Mercuric formate test (IV, 36, 8).

**Oxalate.** (i) Immediate precipitation with  $\text{CaCl}_2$  solution in neutral solution; precipitate decolourises a dilute solution of  $\text{KMnO}_4$  (IV, 37, 3, 4). (ii) Resorcinol test (IV, 37, 5).

**Tartrate.** (i) Resorcinol test (IV, 38, 6). (ii) Copper hydroxide test (IV, 38, 7).

**Citrate.** (i) Denigès' test (IV, 39, 5). (ii) Cadmium chloride solution test (IV, 39, 4), and negative results with resorcinol and copper hydroxide tests (IV, 38, 6, 7).

**Salicylate.** (i) Violet coloration with  $\text{FeCl}_3$  solution, discharged by mineral acids (IV, 40, 5), and soda lime test (IV, 40, 7). (ii) "Oil of winter-green" test (IV, 40, 2).

**Benzoate.** (i) Buff-coloured precipitate with  $\text{FeCl}_3$  solution, soluble in dilute  $\text{HCl}$  with precipitation of benzoic acid (IV, 41, 1). (ii) Dilute  $\text{H}_2\text{SO}_4$  test (IV, 41, 2), and no precipitate with  $\text{BaCl}_2$  solution in neutral solution.

**Succinate.** (i) Light brown precipitate with  $\text{FeCl}_3$  solution, soluble in dilute  $\text{HCl}$ , but no precipitation of acid occurs (IV, 42, 3). (ii) Fluorescein test (IV, 42, 6).

## VII, 18. ANALYSIS OF A LIQUID (SOLUTION)

(1) Observe the colour, odour and any special physical properties.

(2) Test its reaction towards litmus paper or a suitable narrow range indicator paper.

(a) *The solution is neutral*: free acids, free bases, acid salts, and salts which give an acid or alkaline reaction owing to hydrolysis, are absent.

(b) *The solution reacts alkaline*: this may be due to the hydroxides of the alkali and alkaline earth metals, to the carbonates, borates, sulphides, cyanides, hypochlorites, zincates, aluminates, silicates, per-salts and peroxides of the alkali metals, etc.

(c) *The solution reacts acid*: this may be due to free acids, acid salts, salts which yield an acid reaction because of hydrolysis, or to solutions of salts in acids.

(3) Evaporate a known volume of the liquid to dryness on the water bath; carefully smell vapours evolved from time to time. If a solid residue remains, examine as described under A for solid and non-metallic substances (Section VII, 1). If a liquid remains, evaporate cautiously on a wire gauze in the fume cupboard; a solid residue should be examined as already stated. If charring occurs, organic matter is present, and must be removed before testing for Group IIIA in the subsequent systematic analysis. If no residue remains, then the liquid consists of some volatile substance which may be water or water containing certain gases or volatile substances, such as  $\text{CO}_2$ ,  $\text{NH}_3$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{H}_2\text{O}_2$ ,  $(\text{NH}_4)_2\text{CO}_3$ , etc., all of which can be readily detected by special tests. It is best to neutralise the solution with sodium carbonate and test for acid radicals (anions).

(4) If the solution reacts alkaline, the following tests should be performed:

(a) **Peroxides and per-salts** (e.g.  $\text{H}_2\text{O}_2$  and  $\text{NaBO}_3$ ).

(i) Heat a little of the solution with a few drops of cobalt nitrate solution; a black precipitate of a higher oxide of cobalt is obtained (sulphides and hypochlorites interfere and must be absent).

(ii) Add a little titanous sulphate or chloride solution, and carefully acidify with cold dilute sulphuric acid; a yellow coloration is obtained in the presence of hydrogen peroxide.

(iii) Add a little ferric chloride and potassium ferricyanide solutions; Prussian blue precipitate.

(b) **Hydroxides and carbonates.** Boil to decompose hydrogen peroxide, if present. Add a slight excess of barium chloride solution; if the solution now reacts alkaline, hydroxyl ions are present. Filter off the precipitate, and examine for carbonate with dilute acid (Section IV, 2, reaction 1).

(5) If the original solution is acidic, render a known volume (say, 5 ml.) alkaline with aqueous ammonia before evaporating it on a water bath. This will prevent the loss of volatile acids, such as hydrochloric and boric acids. Examine the residue.

## VII, 19. ANALYSIS OF A METAL OR AN ALLOY

The analysis of a metal or of an alloy is simplified by the fact that no acid radicals or anions need be looked for. Many alloys contain small amounts of P, Si, C and S; phosphorus is converted by the usual solution process into phosphate, and may be identified as such (Section IV, 28).

The alloy or metal should be in the form of borings, turnings or filings. About 0.5 gram is treated with 10 ml. of concentrated nitric acid in a porcelain basin in the fume chamber, warmed gently until the evolution of red fumes ceases, and evaporated almost to dryness.\* About 10 ml. of water are then added, the mixture heated for a few minutes and filtered, if necessary.

Three cases may arise:

1. **The metal or alloy dissolves completely.** Examine solution (A) by Table I (Section VII, 6), remembering that phosphate may be present and should be tested for.

2. **The metal or alloy does not dissolve completely.** The solution (A) is examined as in case 1. If the residue is black, it may be either carbon or gold and/or platinum. Test for carbon by igniting on a crucible lid; carbon glows and burns. Gold and platinum dissolve in aqua regia (compare Sections IX, 5 and IX, 6).

If the residue is white, it may contain *inter alia* hydrated stannic oxide or antimony pentoxide, bismuth oxide, together with traces of copper, lead and iron, and is best analysed as outlined in the following table.

\* The nitric acid will oxidise the P to  $H_3PO_4$ , S to  $H_2SO_4$ , As to  $H_3AsO_4$ , Sb to  $Sb_2O_5 \cdot xH_2O$  (converted by gentle heating into  $Sb_2O_5$ ), Sn to  $SnO_2 \cdot xH_2O$  and Si to gelatinous silicic acid.

**Table XII.—Analysis of Portion of Alloy Insoluble in Concentrated Nitric Acid**

Wash residue with water, and dry by heating in a crucible. Add 6 times its weight of an intimate mixture of equal parts of anhydrous  $\text{Na}_2\text{CO}_3$  and sulphur, mix well, cover the crucible and heat over a small flame until the excess of sulphur has burned off. This operation usually occupies about 20 minutes. Allow to cool and extract contents of the crucible with hot water and filter.

**Residue.** May contain  $\text{PbS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{CuS}$  and  $\text{FeS}$ . Dissolve in hot dilute  $\text{HNO}_3$ , filter off any  $\text{S}$  and evaporate almost to dryness. Dissolve in water and add to original solution A.

**Filtrate.** May contain  $\text{Na}_2\text{SnS}_3$ ,  $\text{Na}_3\text{SbS}_4$ ,\*  $\text{Na}_3\text{AsS}_4$ ,  $\text{Na}_3\text{PO}_4$  and, possibly,  $\text{Na}_2\text{S}$ . Acidify with dilute  $\text{HCl}$  (test with litmus paper), and filter.

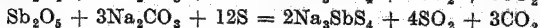
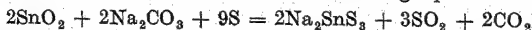
**Residue.** May contain  $\text{SnS}_2$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{As}_2\text{S}_3$  and  $\text{S}$ . Examine by Tables VI or VII (Section VII, 11) for  $\text{As}$ ,  $\text{Sb}$  and  $\text{Sn}$ .

**Filtrate.** Test for phosphate. Boil off  $\text{H}_2\text{S}$ , add excess of  $\text{NH}_3$  solution and then magnesium nitrate reagent. A white crystalline ppt. indicates phosphate present. Confirm.

3. The metal or alloy is unattacked. If the alloy is not attacked by nitric acid (1 : 1), treat a separate 0.5 gram sample with 20 ml. of aqua regia (15 ml. of concentrated hydrochloric acid and 5 ml. of concentrated nitric acid) in a porcelain dish. Cover the latter with a clock glass and heat gently until the alloy has disintegrated completely. Raise the clock glass, boil down to about 5 ml. and finally evaporate to dryness on a water bath. Add 5 ml. of concentrated hydrochloric acid, heat gently, dilute with 15 ml. of water, stir and heat to boiling. Cool to room temperature and filter. The residue may consist of  $\text{AgCl}$ ,  $\text{PbCl}_2$  and  $\text{SiO}_2$ . The filtrate may contain the metals of the remaining Groups together with arsenate, orthophosphate and sulphate. Examine by Table I (Section VII, 6).

If the alloy resists the action of aqua regia, fuse it with sodium hydroxide pellets in a silver dish or crucible (*CAUTION!*). When decomposition is complete, allow to cool, transfer the silver vessel to a beaker and extract the melt with water; remove the silver vessel from the beaker. Strongly acidify the

\* These are formed in accordance with the following equations:



contents of the beaker with nitric acid, evaporate to dryness on a water bath and proceed as above.

The alkali fusion is sometimes replaced by warming on a water bath with concentrated hydrochloric acid and 10–20 per cent of its volume of liquid bromine.

The compositions of some of the common alloys are given in Table XIII; the chief constituents are listed in the order of their predominance.

Table XIII. Composition of Alloys

Brasses	Cu, Zn, Sn, Pb
Bronzes	Cu, Sn, Zn, Pb
Phosphor bronzes	Cu, Sn, Pb, P
Solders	Sn, Pb, Bi
Pewter	Sn, Sb, Pb, Cu
Type metals	Pb, Sb, Sn
German silver	Cu, Ni, Zn
Monel metal	Ni, Cu
Constantan	Cu, Ni
Nichrome	Ni, Fe, Cr
Manganin	Cu, Mn, Ni
Wood's alloy	Bi, Pb, Sn, Cd
Rose's alloy	Bi, Pb, Sn

## VII, 20. ANALYSIS OF INSOLUBLE SUBSTANCES

A substance which cannot be dissolved by concentrated acids (hydrochloric or nitric) or by aqua regia is described as "insoluble." Special methods for solution must therefore be employed, the actual process chosen depending largely upon the nature of the insoluble substance.

The most common insoluble substances encountered in qualitative analysis are:

$\text{AgCl}$ ,  $\text{AgBr}$ ,  $\text{AgI}$ ,  $\text{AgCN}$ ;

$\text{SrSO}_4$ ,  $\text{BaSO}_4$ ,  $\text{PbSO}_4$ ;

the strongly ignited oxides  $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{SnO}_2$ ,  $\text{Sb}_2\text{O}_4$ ,  $[\text{TiO}_2, \text{ThO}_2, \text{WO}_3 \cdot x\text{H}_2\text{O}]$ ;

fused  $\text{PbCrO}_4$ , and certain minerals, *e.g.*  $\text{CaF}_2$  (fluor spar),  $\text{FeCr}_2\text{O}_4$  (chrome ironstone);

$\text{Cu}_2[\text{Fe}(\text{CN})_6]$ ,  $\text{Zn}_2[\text{Fe}(\text{CN})_6]$ , Prussian blue;

$\text{SiO}_2$ , and various silicates;  $\text{SnS}_2$  (mosaic gold); C and S; metallic silicides; carborundum.

The insoluble substance should be subjected to the tests enumerated below in the order given until it is brought into solution. (Some of these tests will have been carried out in the preliminary examination.) The substance should be in the form of a fine powder; use an agate mortar, if necessary.

**(1) Note colour and appearance.**

The following substances are coloured:  $\text{Cr}_2\text{O}_3$  (green),  $\text{Fe}_2\text{O}_3$  (dark red),  $\text{SnS}_2$  (bronze),  $\text{PbCrO}_4$  (brown),  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  (Prussian blue),  $\text{Cu}_2[\text{Fe}(\text{CN})_6]$  (dark brown),  $\text{FeCr}_2\text{O}_4$  (dark grey),  $\text{AgBr}^*$  (very pale yellow),  $\text{AgI}^*$  (light yellow), C and S.

The remaining substances listed above are white or nearly so, but may be slightly coloured by traces of impurities; the effect of the latter is less marked when the substance is in the form of a fine powder.

**(2) Examine the effect of heat.**

Heat a small quantity in a small crucible or upon platinum foil. Sulphur will melt to a yellow liquid, and burn with a blue flame with the production of sulphur dioxide (test with potassium dichromate paper or with fuchsin solution).

Carbon will glow and burn away almost completely; a light-coloured ash may remain. If the black substance is dropped in *very small quantities* into a little fused potassium nitrate contained in a hard glass tube, the oxidation will be more vigorous and some potassium carbonate will be formed. The residue will evolve carbon dioxide on treatment with dilute acids. Additional confirmation of carbon is obtained by heating an intimate mixture of the substance with dry cupric oxide in a hard glass tube; carbon dioxide will be evolved (test with lime water), and red metallic copper will remain.



The silver salts,  $\text{AgCl}$ ,  $\text{AgBr}$  and  $\text{AgI}$ , will melt without further change;  $\text{AgCN}$  decomposes to give a residue of silver, and cyanogen gas is evolved.

Antimony oxide  $\text{Sb}_2\text{O}_4$  melts to a yellow liquid.

**(3) Heat with sodium carbonate upon charcoal.**

The following observations may be made:

(a) No metallic button is produced. This indicates the absence of Ag, Sn and Pb. Either moisten residue with a few drops of dilute hydrochloric acid and place in contact with lead

\* The silver halides become violet on exposure to light.

acetate paper or extract with a little water and filter into freshly prepared sodium nitroprusside solution; a black stain or a transient violet coloration respectively indicates the presence of sulphide and therefore of *sulphate* in the original substance.

The test should be repeated with another portion of the original substance if a white residue is obtained. Add one or two drops of cobalt nitrate solution and heat again. A blue mass indicates *aluminium*.

(b) A metallic button or bead is obtained. The solubility of the bead in nitric acid and in hydrochloric acid is tested.

- (i) The bead dissolves in nitric acid forming a clear solution, and yielding a curdy, white precipitate of silver chloride, soluble in dilute ammonia solution, upon the addition of a little hydrochloric acid. The presence of *silver* and the absence of tin is indicated.
- (ii) The bead gives a clear solution with hydrochloric acid, and the addition of mercuric chloride solution produces a white precipitate of mercurous chloride. With nitric acid, a white insoluble powder ("metastannic acid") is produced. This test indicates the presence of *tin* and the absence of silver.

#### (4) Heat with concentrated sulphuric acid.

- (i) Escaping gas renders a drop of water upon a glass rod turbid. *Fluoride* is indicated.
- (ii) Carbon monoxide evolved, which burns with a blue flame. *Ferrocyanide* is indicated.

#### (5) Heat upon a platinum wire in the reducing zone of the Bunsen flame.

This process will reduce any sulphate present to sulphide (as already indicated in test 3). Upon moistening with dilute hydrochloric acid, the sulphide will be converted into the comparatively volatile chloride, and the usual flame test is applied. The presence of *barium* or of a mixture of *strontium* and *barium* will be indicated.

#### (6) Apply the microcosmic bead test.

If a skeleton bead is obtained, *silica* or a *silicate* is indicated. A negative result does not definitely prove that silica or a silicate is absent, as a skeleton is not always formed. The silicon tetrafluoride test should then be employed (Section IV, 26, reaction 6).



Heat the bead in the reducing flame in order to test for *titanium*. If the bead is violet when cold (the colour is produced more readily by the addition of a minute speck of tin or of stannous chloride), the presence of titanium is indicated. If iron is also present, the bead will be coloured brownish-red in the reducing flame.

When titanium is found, it is best to fuse with potassium pyrosulphate in a silica or platinum crucible, and to extract the residue with *cold* water whereby a solution of titanic sulphate is obtained.

#### (7) Heat with sodium carbonate and potassium nitrate.

This test may be carried out in a loop of platinum wire or upon platinum foil or upon a piece of broken porcelain. If *chromium* is present, a yellow melt is produced. This should be dissolved in water, acidified with dilute acetic acid, and (a) silver nitrate solution added, when brownish-red silver chromate is precipitated, (b) lead acetate solution added, when yellow lead chromate is precipitated, or (c) 1-2 ml. of diphenyl-carbazide reagent added, when a deep red coloration is produced.

#### (8) Boil with sodium hydroxide solution.

✱ (i) Lead chromate dissolves:



(ii) Prussian blue yields ferric hydroxide and sodium ferrocyanide (see under Iron, Section III, 20, reaction 5).

(iii) Copper ferrocyanide yields copper oxide and sodium ferrocyanide.

(iv) Zinc ferrocyanide yields sodium zincate and sodium ferrocyanide, *i.e.* it dissolves completely. The zinc is readily identified by passing hydrogen sulphide into the solution; the ferrocyanide (see Section IV, 11) is detected in the filtrate after acidifying and boiling off the hydrogen sulphide.

(v) Alumina and silica may dissolve, forming solutions of sodium aluminate and sodium silicate respectively.

#### ✓ (9) Heat with concentrated hydriodic acid.

The powdered substance (0.5 gram) should be heated to just below the boiling point with hydriodic acid, sp. gr. 1.7\* (2.5 ml.).

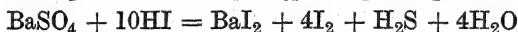
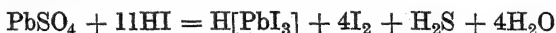
\* Where colour reactions are to be observed, it is recommended that the hydriodic acid be decolourised by the addition of 1-2 per cent by volume of 50 per cent hypophosphorous acid or by warming with a little potassium hypophosphite.

(i) Stannic oxide dissolves. A pink to red coloration is produced when the solution cools; the coloration disappears on warming to 90–100°C. A yellow to orange sublimate of stannic iodide is frequently observed.



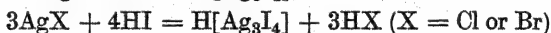
Upon filtration and dilution, the tin may be precipitated with hydrogen sulphide.

(ii) The sulphates of lead, strontium and barium are gradually decomposed and hydrogen sulphide is evolved, which is identified by ammoniacal sodium nitroprusside paper (see under Sulphides, Section IV, 6, reaction 6).



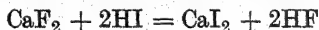
Upon filtration through a sintered glass crucible and dilution, golden yellow lead iodide is precipitated from lead sulphate. Barium may be detected by the addition of dilute sulphuric acid, and strontium by sulphuric acid and ethyl alcohol.

(iii) The silver halides dissolve readily in the *cold*, owing to complex formation:



Upon warming the solution, the hydrogen halides are expelled from solution with effervescence. When the solution is diluted, the complex iodo-argentous acid is decomposed and silver iodide is precipitated; it is best, however, to expel the excess of hydriodic acid by evaporation before diluting with water. If lead sulphate was originally present, lead iodide will be precipitated on dilution; this can be separated from silver iodide by extraction with ammonium acetate solution.

(iv) Calcium fluoride is attacked by the hot acid, hydrogen fluoride being evolved, which will etch glass:



Upon dilution, neutralisation with ammonia solution and addition of ammonium oxalate solution, the calcium is precipitated as calcium oxalate.

#### (10) Treat with ammonium sulphide solution.

If the insoluble unknown or the washed residue from the aqua regia extraction is white or light-coloured, treat it in a porcelain dish or crucible with a few drops of ammonium sulphide solution and stir. Lead and silver compounds are

probably absent if the colour is unchanged. A blackening of the solid indicates that lead and silver compounds may be present.

### ✓ PREPARING A SOLUTION

The above preliminary tests may supply valuable information as to the composition of the insoluble substance. In every case, the following methods of bringing the substance into solution for systematic analysis should be used.

#### (a) Removal of lead salts.

Treat about 1 gram of the insoluble unknown, or the residue from the aqua regia extraction, with 3 ml. of concentrated ammonium acetate solution slightly acidified with acetic acid. (Excess of ammonia solution must be absent to avoid the solvent action upon any silver chloride which may be present.) Heat the mixture, with stirring, to about  $70^{\circ}\text{C}$  and filter; wash with about 5 ml. of water. Test separate portions of the combined filtrate and washings for  $\text{Pb}^{++}$ ,  $\text{SO}_4^{--}$  and  $\text{Cl}^-$ . The silver nitrate test for chloride must be conducted in the presence of about 10 per cent of the volume of concentrated nitric acid and the mixture heated to boiling; silver acetate will dissolve under these conditions. If lead salts are found, repeat the extraction with ammonium acetate solution and wash the residue with hot water until the washings give no coloration with dilute ammonium sulphide solution.

Lead silicate is insoluble in ammonium acetate solution; it will be detected in (c).

#### (b) Removal of silver salts.

Warm the insoluble unknown or the residue from (a) (if lead salts are present) with a concentrated solution of potassium cyanide. (If it dissolves completely, only  $\text{AgCl}$ ,  $\text{AgBr}$ ,  $\text{AgI}$  and  $\text{AgCN}$  are present.) Filter and reserve the residue *R* for subsequent treatment. Dilute the filtrate considerably and treat with hydrogen sulphide. Filter off any black precipitate ( $\text{Ag}_2\text{S}$ ), wash, dissolve in hot dilute nitric acid and add dilute hydrochloric acid. A white precipitate of silver chloride indicates the presence of *silver*.

If silver is found, the halogen with which the metal was originally combined is identified by melting another portion of the insoluble substance, immersing it in dilute sulphuric acid, placing a piece of zinc in contact with the acid and the fused mass, warming and allowing to stand for a few minutes. The

silver salt is reduced to metallic silver, whilst the acid radicals (anions) are present in solution in the presence of zinc ions, *i.e.* as zinc salts. Filter. The filtrate is tested for chloride, bromide and iodide in the usual manner; the tests for mixtures of these anions are described in Section IV, 45, and in Section VII, 16, Table A.

### (c) Sodium carbonate fusion.

The residue *R*, free from lead and silver salts, or the original substance, if lead and silver salts are absent, is mixed with 5–6 times its weight of pure, sulphate-free, anhydrous  $\text{Na}_2\text{CO}_3$  or with a mixture of equal parts of  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  (fusion mixture). The mixture is heated upon Pt foil or in a Ni crucible until a tranquil melt is obtained. (It may be necessary to heat over the blowpipe flame.) Allow to cool, extract the melt thoroughly by boiling it with water. Filter.

**Residue.** Wash well, first with 2%  $\text{Na}_2\text{CO}_3$  solution, and then with hot water. May contain *inter alia*  $\text{BaCO}_3$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ , other insoluble carbonates and unattacked  $\text{CaF}_2$ ,  $\text{SnO}_2$ ,  $\text{Sb}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , etc.

Extract with dilute  $\text{HNO}_3$ , and filter.

**Filtrate.** May contain  $\text{Na}_2\text{CrO}_4$ ,  $\text{Na[AlO}_2]$ ,  $\text{Na}_2[\text{SnO}_3]$ ,  $\text{Na}_2\text{AsO}_4$ ,  $\text{NaF}$ ,  $\text{Na}_2\text{SO}_4$  and the corresponding K salts, if fusion mixture was employed. Acidify with concentrated  $\text{HCl}$  and evaporate to dryness in the fume cupboard. Triturate the dry mass with concentrated  $\text{HCl}$ , add water, warm and filter.

**Residue.** If white, may contain  $\text{CaF}_2$ ,  $\text{SnO}_2$ ,  $\text{Sb}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , etc., which are incompletely attacked by  $\text{Na}_2\text{CO}_3$ . Fuse with  $\text{NaOH}$  in a Ni crucible.\* Allow to cool, extract with water and filter. The filtrate may contain sodium stannate, sodium antimonate, sodium aluminate and sodium silicate.

Test for Sn, Sb and Al.

**Filtrate.** Evaporate almost to dryness to remove  $\text{HNO}_3$ , add dilute  $\text{HCl}$  and examine for metal ions by Table I (Section VII, 6).

**Residue.** May contain  $\text{SiO}_2$ .† Confirm by microcosmic bead test or by the  $\text{SiF}_4$  test in a lead capsule.

**Filtrate.** Test a portion for sulphate. Examine for metals of Groups II and III.

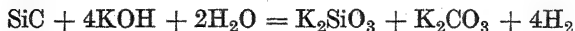
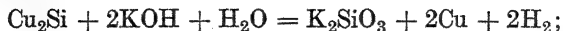
**Metallic silicides and carborundum** are rarely encountered in routine qualitative analysis. They are best brought into

\* An alternative procedure is the  $\text{Na}_2\text{CO}_3$ -S fusion method already described under the analysis of metals and alloys (Table XII, Section VII, 19).

The original insoluble substance may also be subjected to the  $\text{Na}_2\text{CO}_3$ -S fusion, and the extract, after acidifying with 1 : 1  $\text{HCl}$ , filtered. Any precipitate is washed, dissolved in concentrated  $\text{HCl}$  and  $\text{H}_2\text{S}$  removed by boiling: Sb may be detected with Rhodamine-B and Sn with  $\text{HgCl}_2$  solution.

† This precipitate may also contain  $\text{WO}_3 \cdot x\text{H}_2\text{O}$  from mineral tungstates insoluble in aqua regia. Confirm W by digesting with dilute  $\text{NH}_3$  solution to dissolve  $\text{WO}_3 \cdot x\text{H}_2\text{O}$  and then apply the  $\text{SnCl}_4$ - $\text{HCl}$  test.

solution by fusion with sodium or potassium hydroxide in a silver crucible (*CAUTION!*):



During the fusion the liberated hydrogen catches fire forming water by combination with the oxygen of the air. Upon treating the melt with water, the soluble potassium silicate, etc., is extracted.

• • **Carborundum** when in the form of a fine powder is readily decomposed by fusion with potassium carbonate in a platinum crucible. Upon removing the cover of the crucible the blue flame of burning carbon monoxide may be seen.



## CHAPTER VIII

### MODIFICATION OF THE SYSTEMATIC ANALYSIS WHEN ORGANIC ACIDS, SILICATES, BORATES, FLUORIDES AND PHOSPHATES ARE PRESENT

REFERENCE has already been made in Chapter VII, Tables I and II, to the modification of the analysis after Group II necessitated by the presence of various interfering acid radicals (anions). It is the express purpose of this Chapter to discuss this subject in greater detail in order that the student may understand the reason for each operation, and also to indicate alternative procedures whereby some of the interfering radicals may be removed.

The interfering acid radicals may be divided into two main groups:

(i) Those which, when present in solution, combine with various metals to form stable complex ions (compare Section I, 20); this may result in the failure of these metals to precipitate with the usual group reagent. To this class belong such organic acids as oxalic, citric and tartaric acids, and also hydroxy compounds, such as sugar and starch. In their presence, iron, chromium and aluminium are either incompletely precipitated or not precipitated at all by ammonium chloride and ammonia solution.

(ii) Those which, under certain conditions, form insoluble compounds with some of the metals of the later groups. It is conceivable, therefore, that under conditions which result in the precipitation of the Group IIIA metals, metals of the subsequent groups will also be precipitated in consequence of the formation of compounds which are insoluble or sparingly soluble in the presence of ammonium chloride and ammonia solution. The most important of these acid radicals are oxalates, tartrates, citrates, borates, fluorides and phosphates. Silicates are included with these owing to the precipitation of gelatinous silicic acid by ammonium chloride and ammonia solution (see under Silicates, Section IV, 26, reaction 2).

Reference to a table of solubilities will show:

(a) That the oxalates, tartrates and citrates of most of the metals of Groups IIIA, IIIB and IV and of magnesium are

either insoluble or difficultly soluble in water. (It should be noted that most oxalates and tartrates, with the exception of those of calcium, strontium and barium, form soluble complex salts with alkali oxalates and alkali tartrates respectively; compare (i) above.)

(b) That the borates of the metals of Groups IIIA, IIIB and IV are insoluble in water; magnesium borate is sparingly soluble. (Some of these are, however, soluble in ammonium chloride solution.)

(c) That the fluorides of calcium and magnesium are insoluble, and those of nickel, cobalt, strontium and barium are sparingly soluble in water.

(d) That the phosphates of the metals of Groups IIIA, IIIB, IV and of magnesium are insoluble in water.

Furthermore, the borates, fluorides, phosphates, oxalates, tartrates and citrates of the Group IIIA, IIIB and IV metals and of magnesium are insoluble in alkaline solution, but dissolve in acid solution.

It is evident that in the presence of these acids, Group IIIA metals cannot be separated from those of the remaining groups by the addition of the customary group reagent,  $\text{NH}_4\text{Cl}$  and  $\text{NH}_3$  solution. The usual scheme of systematic analysis is therefore modified when any or all of these anions are present before proceeding to the precipitation of Group IIIA.

The presence of some of these anions will have been indicated in the preliminary tests. Organic acids are revealed in the dry tests, and particularly by the action of concentrated sulphuric acid. In view of the common occurrence of oxalates and the somewhat indecisive indications of the preliminary tests, it is recommended that this radical be tested for in a portion of the filtrate from Group II, from which all the hydrogen sulphide has been expelled by boiling. This is most simply carried out by adding 1 ml. of  $\text{CaCl}_2$  solution and 1 ml. of  $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$  solution to 1 ml. of the solution; if a *crystalline* precipitate forms (the precipitate should not be confused with *gelatinous*  $\text{CaF}_2$ ), filter, wash, dissolve in a little hot dilute  $\text{H}_2\text{SO}_4$ , filter and add 2-3 drops of dilute  $\text{KMnO}_4$  solution to the filtrate. If the colour of the  $\text{KMnO}_4$  solution is discharged, an *oxalate* is present.

The presence of *fluoride* is indicated in the preliminary treatment with concentrated sulphuric acid; a moistened glass rod introduced into the tube becomes covered with a film of gelatinous silicic acid.

The detection of *borate* is provided for in the preliminary

test (ix) of Section VII, 3. Alternatively, it may be tested for after the precipitation of Group II.

The presence of *phosphate* is always tested for in the Group II filtrate, from which all the  $\text{H}_2\text{S}$  has been expelled. To 1 ml. of the solution, add 1 ml. of  $\text{HNO}_3$  and 3 ml. of ammonium molybdate solution, and warm to a temperature not exceeding  $40^\circ$ . The production of a bright yellow precipitate proves the presence of a phosphate (Section IV, 28, reaction 4).

### VIII, 1. PROCEDURE FOR THE REMOVAL OF INTERFERING ACIDS IN SYSTEMATIC QUALITATIVE ANALYSIS

The acids are removed in the following order:

**1. Organic acids.** The filtrate from Group II is evaporated to dryness, when some carbon may be liberated and the organic acids decomposed. By repeated evaporation with concentrated  $\text{HNO}_3$ , the black residue is completely oxidised. The residue must not be heated too strongly as  $\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  may be rendered very difficultly soluble in  $\text{HCl}$ .

**2. Borates and fluorides.** The residue from 1 is repeatedly evaporated almost to dryness with concentrated  $\text{HCl}$ ; the  $\text{HF}$  volatilises with the  $\text{HCl}$  and the  $\text{H}_3\text{BO}_3$  volatilises in the steam.

If borate is present and fluoride is absent, the former may be removed by repeated evaporation to dryness on a water bath with a mixture of 5 ml. of methyl alcohol (flammable!) and 10 ml. of concentrated  $\text{HCl}$ . The borate slowly volatilises as methyl borate,  $(\text{CH}_3)_3\text{BO}_3$  (*poisonous*).

**3. Silicates.** The evaporation with concentrated  $\text{HCl}$  converts silicates into an insoluble form of  $\text{SiO}_2$ . Hence by complete evaporation to dryness with a further quantity of concentrated  $\text{HCl}$ , extraction with water or dilute  $\text{HCl}$ , and filtration, the silicate is completely eliminated.

**4. Phosphates.** There are several methods for the removal of phosphate ions: one of these, the zirconium nitrate method, has already been outlined in Table II (Section VII, 7). The zirconium nitrate procedure is by far the most convenient; if correctly performed, all phosphate ions are quantitatively and rapidly removed as the highly insoluble zirconium phosphate. All the other "phosphate separations" are tedious and time-consuming, and the quantitative removal of phosphate ions is



not always achieved: they are therefore not recommended for general use. Only one of the alternative procedures will be described in detail, since it incorporates a number of points of theoretical interest and is accordingly of some pedagogic value. Another procedure is described also since it finds application in the presence of the "rarer" elements.

## VIII, 2. ANALYTICAL PROCEDURES IN THE PRESENCE OF PHOSPHATES. "PHOSPHATE SEPARATIONS"

The various procedures which have been proposed for the removal of the interfering phosphate ions in qualitative analysis are all based upon precipitation processes. These include:

- (a) the basic acetate method;
- (b) the ferric chloride method;
- (c) the tin method;
- (d) the stannic chloride method;
- (e) the formate buffer method; and
- (f) the zirconium chloride method;

the last-named is similar, but inferior, to the zirconium nitrate procedure. Only a modification of the basic acetate method and also the stannic chloride method will be described here.\* The former is given in Table I: it is termed the acetate buffer-ferric chloride method. The latter finds application in the removal of phosphates when the so-called "rarer" elements are present in Group IIIA (see Section IX, 18).

\* For details of the other procedures, see the *Third Edition* of this Text Book (1945).

## VIII, 2. Table 1.—Phosphate Separation by the Acetate Buffer- $\text{FeCl}_3$ Method

If a phosphate has been found in Table I (Separation of Cations into Groups, Section VII, 6), proceed as follows. Dissolve the ppt. produced by the action of  $\text{NH}_4\text{Cl}$  and a slight excess of  $\text{NH}_3$  solution in the *minimum* volume of dilute  $\text{HCl}$ . [The ppt. may contain  $\text{Fe}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{Cr}(\text{OH})_3$ ,  $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ , traces of  $\text{CaF}_2$  and the phosphates of Mg and of the Group IIIA, IIIB and IV metals.] Test about 0.5 ml. for Fe by the addition of  $\text{K}_4[\text{Fe}(\text{CN})_6]$  or  $\text{NH}_4\text{SCN}$  solution. To the main volume of the cold solution, add dilute  $\text{NH}_3$  solution dropwise, with stirring, until either a faint permanent precipitate is just obtained or until the solution is just alkaline (test with litmus paper). Then add 2–3 ml. of dilute acetic acid (1 : 1) and 10 ml. of 3*N* ammonium acetate solution. Disregard any ppt. which may form at this stage. If the solution is red or brownish red, sufficient ferric iron is present (1) in the solution to combine with all the phosphate ions. If the solution is not red in colour, add “neutral”  $\text{FeCl}_3$  solution (2), drop by drop and with stirring, until the solution acquires a deep brownish-red colour (3). Dilute the solution to about 150 ml. with hot water, boil gently for 1–2 minutes, filter hot (4) and wash the residue with a little boiling water.

**Residue.** May contain the phosphates (and, possibly, the basic acetates) of Fe, Al and Cr and also  $\text{Fe}(\text{OH})_3$ .

### Group IIIA present.

Rinse the ppt. into a porcelain dish by means of 10 ml. of cold water, add 1–1.5 grams of sodium perborate  $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$  (or add 5 ml. of  $\text{NaOH}$  solution, followed by 5 ml. of 3%  $\text{H}_2\text{O}_2$  solution), and boil gently until the evolution of  $\text{O}_2$  ceases (2–3 minutes). Filter and wash with a little hot water.

**Filtrate.** Boil down in an evaporating dish to 20–25 ml. Add 0.5 gram of  $\text{NH}_4\text{Cl}$  and then dilute  $\text{NH}_3$  solution in slight excess. Filter, if necessary.

**Residue.**  
 $\text{FePO}_4 + \text{Fe}(\text{OH})_3$ .  
Reject.

**Filtrate.** May contain  $\text{NaAlO}_2$  and  $\text{Na}_2\text{CrO}_4$ .  
Examine for Al and Cr as described in Group Separation Table VII (Section VII, 12).

**Residue.**  
Examine for Al and Cr, if not previously tested for.

[In general, no ppt. will be obtained here.]

**Filtrate.**  
Examine for Groups IIIB, IV and for Mg as detailed in General Table I (Section VII, 6).

**Notes.** (1) If the reddish-brown colour cannot be seen owing to the formation of a precipitate or the presence of coloured ions, filter a small portion of the mixture and render the filtrate alkaline with dilute ammonia solution. If a light coloured precipitate is obtained, more ferric chloride solution should be added to the main mixture with stirring until a similar test gives a reddish-brown precipitate, indicating that  $\text{Fe}^{+++}$  is present in excess.

(2) “Neutral”  $\text{FeCl}_3$  solution is prepared by adding dilute ammonia solution dropwise to the side-shelf  $\text{FeCl}_3$  solution until a *slight* permanent precipitate forms; this is filtered off. The side-shelf reagent usually contains excess of free hydrochloric acid added

during its preparation to produce a clear solution; the free acid leads to incomplete precipitation.

(3) If the colour cannot be seen because of the presence of a precipitate or of coloured ions, filter a small portion of the mixture and test the filtrate with dilute ammonia solution as in *Note 1*. A large excess of  $\text{FeCl}_3$  solution must be avoided since it exerts a solvent action on ferric phosphate and the precipitation of the latter will be incomplete.

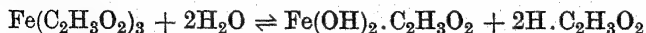
(4) The addition of filter paper pulp or a Whatman filtration accelerator will facilitate filtration.

### *Explanation (Table I)*

The theoretical basis of the acetate buffer- $\text{FeCl}_3$  method may be summarised as follows:

(a)  $\text{FePO}_4$ ,  $\text{AlPO}_4$  and, to a lesser extent,  $\text{CrPO}_4$  are insoluble in warm, dilute acetic acid buffered by a solution of ammonium acetate: the phosphates of the metals of Group IIIB and IV and of Mg are soluble.

(b) The precipitation of phosphate ions will be complete only if the trivalent ions are present in excess. The procedure depends upon having excess of ferric ions present. Ferric iron is chosen because (i) it is easy to test for  $\text{Fe}^{+++}$  in the filtrate from Group II, (ii) ferric phosphate is the least soluble in the acetic acid medium and (iii) it can most easily be detected by its colour in aqueous solution. Furthermore, the excess of ferric ions can be readily removed since ferric acetate is considerably hydrolysed upon dilution and boiling, and the excess of iron is precipitated as basic ferric acetate (or as ferric hydroxide occluding large amounts of acetate ions).



The reaction tends to reverse upon cooling, hence filtration of the hot solution is desirable.

(c) The addition of ammonium acetate solution to a solution containing iron, aluminium and chromium ions yields the acetates of these metals: upon boiling the highly diluted solutions, the basic acetate of iron is almost completely and that of aluminium is largely precipitated. Chromium acetate does not appear to form a basic acetate under these conditions, but in the presence of considerable quantities of iron and aluminium, chromium is coprecipitated to a considerable extent with these two elements either as the basic acetate or as an adsorption complex.

**Phosphate separation by the stannic chloride method.**

—It has been found that a freshly prepared solution of stannic chloride readily removes phosphates from solution. It is highly probable that the phosphate is removed largely as the insoluble stannic phosphate  $\text{Sn}_3(\text{PO}_4)_4$ ; an alternative view is that an adsorption complex of phosphoric acid and hydrated stannic oxide is formed, but it may well be that both compound formation and adsorption play a part. When small amounts of phosphates are present, the precipitate filters with difficulty and the filtrate may be turbid; in such cases the addition of more phosphate, say as diammonium phosphate  $(\text{NH}_4)_2\text{HPO}_4$ , to the solution before precipitation with the reagent is recommended.

The experimental procedure is as follows. Boil the filtrate from Group II to remove hydrogen sulphide, dilute to 50 ml., add 3 ml. of 5 per cent diammonium phosphate solution (if necessary), followed by dilute ammonia solution until the precipitate which forms initially does not redissolve on shaking. (The pH should be 3.5–4; the use of congo red or bromophenol blue indicator paper is advantageous.) Add 1 ml. of dilute hydrochloric acid, heat to boiling and introduce 2 ml. of the stannic chloride reagent (prepared by dissolving 5 grams of the crystalline salt in 5 ml. of water). Filter 1–2 ml. of the suspension and test the filtrate for phosphate with ammonium molybdate and nitric acid. If the test is positive, add a further 0.5 ml. of the stannic chloride reagent to the boiling suspension; repeat the process until the phosphate test is negative. Introduce a Whatman filtration accelerator and filter the boiling suspension, preferably with the aid of suction (compare Section II, 2, 10); wash well with hot water. Treat the filtrate and washings with 1 ml. of dilute hydrochloric acid and pass hydrogen sulphide until the precipitation of stannic sulphide is complete. Filter. Concentrate the filtrate and examine it for Groups IIIA, IIIB, IV and V in accordance with the General Table I (Section VII, 6).

If the stannic phosphate precipitate is green in colour, chromium may be present. Boil a small portion of the precipitate with sodium hydroxide solution, allow to cool and add a little hydrogen peroxide solution and 1–2 ml. of amyl alcohol: a blue coloration of the amyl alcohol layer confirms chromium.

## CHAPTER IX

### REACTIONS OF SOME OF THE "RARER" ELEMENTS

No reference has been made in the earlier chapters to the characteristic reactions of the so-called "rarer" elements. Many of these, *e.g.* tungsten, molybdenum, titanium, uranium and beryllium, have important industrial applications, and it was felt that a brief account of the analytical chemistry of a number of selected elements might usefully be included in this volume.

The term "rarer" elements as originally employed in the sense of their comparative rare occurrence and limited availability must now, in a number of cases, be regarded as a misnomer. Large quantities of some of these elements are utilised annually, and the range of the application is slowly but surely widening. A few examples may be mentioned: the use of molybdenum, tungsten, titanium and beryllium in the steel industry, of tungsten in the manufacture of incandescent lamps and of titanium and uranium in the paint industry. The interpretation of the term "rarer" elements, as applied to the elements described in this chapter, is perhaps best accepted in the sense of their comparatively rare occurrence in routine qualitative analysis.

No attempt has been made to give more than a short introduction to the subject; to economise in space, most of the simple equations have been omitted. The elements have been classified, in so far as is possible, in the simple Groups with which the student is already familiar, and methods of separation have been briefly indicated. Thus thallium and tungsten are in Group I; molybdenum, gold, platinum, selenium, tellurium and vanadium in Group II; and beryllium, titanium, uranium, thorium and cerium in Group III. The presence of vanadium will be revealed by the blue colour and absence of precipitate produced by hydrogen sulphide in acid solution; its actual isolation as sulphide is effected by the addition of acid to the ammonium sulphide solution in Group IIIB. It is hoped that the subject-matter of this chapter will suffice to enable the student to detect the presence of one or two of the compounds of the "rarer" elements in a mixture.\*

#### THALLIUM, Tl

Thallium forms two oxides  $Tl_2O$  and  $Tl_2O_3$ , which corresponds to the thallous thallic and salts respectively. The thallous salts are the more stable and hence

\* Such knowledge is required of students preparing for the Associateship of the Royal Institute of Chemistry, the Fellowship of the Royal Institute of Chemistry in Inorganic and in Analytical Chemistry and for certain University examinations.

of greater interest from the analytical viewpoint. Thallous salts are comparatively unstable and readily hydrolyse in solution: thus, when an aqueous solution of thallous sulphate or nitrate is boiled thallous hydroxide is precipitated. Thallous salts are oxidised to thallic by potassium permanganate, potassium ferricyanide, lead dioxide, bromine, chlorine and *aqua regia* (but not by concentrated nitric acid). The reduction of thallic to thallous compounds is easily effected by stannous chloride, sulphurous acid, ferrous salts, or hydroxylamine.

## IX, IA. REACTIONS OF THALLOUS COMPOUNDS

Use a solution of thallous nitrate,\*  $\text{TlNO}_3$  or of thallous sulphate,  $\text{Tl}_2\text{SO}_4$ . [All compounds of thallium are *highly poisonous*.]

1. **Dilute Hydrochloric Acid:** white precipitate of thallous chloride  $\text{TlCl}$ , sparingly soluble in cold, but more soluble in hot water (compare lead).

2. **Potassium Iodide Solution:** yellow precipitate of thallous iodide  $\text{TlI}$ , almost insoluble in water; it is also insoluble in cold sodium thiosulphate solution (difference and method of separation from lead).

† The spot-test technique is as follows. Place a drop of the faintly acid test solution on a black spot plate or upon a blackened watch glass. Add a drop of 10 per cent potassium iodide solution and, when a precipitate appears, a drop or two of 2 per cent sodium thiosulphate solution. A yellow precipitate is produced.

Sensitivity: 0.6  $\mu\text{g}$ .  $\text{Tl}$ . Concentration limit: 1 in 80,000.

The potassium iodide removes mercury as potassium mercuri-iodide  $\text{K}_2[\text{HgI}_4]$ , whilst the sodium thiosulphate dissolves lead and silver as complex thiosulphates.

3. **Potassium Chromate Solution:** yellow precipitate of thallous chromate  $\text{Tl}_2\text{CrO}_4$ , insoluble in cold, dilute nitric or sulphuric acid.

4. **Hydrogen Sulphide:** no precipitate in the presence of dilute mineral acid. Incomplete precipitation of black thallous sulphide  $\text{Tl}_2\text{S}$  occurs in neutral or acetic acid solution.

5. **Ammonium Sulphide Solution:** black precipitate of thallous sulphide  $\text{Tl}_2\text{S}$ , soluble in mineral acids. The precipitate is oxidised to thallous sulphate  $\text{Tl}_2\text{SO}_4$  upon exposure to air.

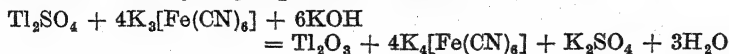
Owing to the slight solubility of thallous chloride, some of the thallium is also precipitated in Group IIIB (compare lead). It is often, however, precipitated with Group II ions.

6. **Sodium Cobaltinitrite Solution:** light-red precipitate of thallous cobaltinitrite  $\text{Tl}_3[\text{Co}(\text{NO}_2)_6]$ .

\* Test solutions containing 10 milligrams per ml. of the reactive anion or required the "rarer elements" should be prepared by the student when cation of (compare Section A, 3); a volume of 5–10 ml. will usually suffice. All the tests can be conveniently conducted on the semimicro scale.

**7. Chloroplatinic Acid Solution:** pale-yellow precipitate of thallic chloroplatinate  $Tl_2[PtCl_6]$ , almost insoluble in water (solubility, 0.06 gram per litre at  $15^\circ$ ).

**8. Potassium Ferricyanide Solution:** brown precipitate of thallic hydroxide,  $Tl(OH)_3$  or  $Tl_2O_3 \cdot xH_2O$ , in alkaline solution. A similar result is obtained with sodium hypochlorite or hypobromite solution or with hydrogen peroxide in alkaline solution.



**9. Ammonium Thiocyanate Solution:** white precipitate of thallic thiocyanate,  $TlSCN$ ; the precipitate is soluble in hot water.

## IX, 1B. REACTIONS OF THALLIC COMPOUNDS

Use a solution of thallic chloride  $TlCl_3$ , prepared by dissolving thallic oxide or thallic hydroxide in moderately concentrated hydrochloric acid.

**1. Sodium Hydroxide or Ammonia Solution:** brown precipitate of thallic hydroxide, insoluble in excess of the reagent (difference from thallic salts, which give no precipitate), but readily soluble in hydrochloric acid.

**2. Hydrochloric Acid:** no precipitate (difference from thallic salts).

**3. Potassium Chromate Solution:** no precipitate (difference from thallic salts).

**4. Potassium Iodide Solution:** brownish-black precipitate, probably a mixture of thallic iodide and iodine.

**5. Hydrogen Sulphide:** reduced to the thallic state with the precipitation of sulphur. If the acid is neutralised, thallic sulphide  $Tl_2S$  precipitates.

### Dry Test.

All thallium salts impart an intense green coloration to the Bunsen flame. This is best identified (and distinguished from barium) with the aid of the spectroscope (see Fig. II, I, 5).

**Separation.**—The element may be precipitated as  $TlCl$  in Group I, separated from  $AgCl$  and  $Hg_2Cl_2$  by solution in boiling water, and from  $PbCl_2$  by means of dilute  $H_2SO_4$ ; the thallium can then be precipitated as  $TlI$  by the addition of  $KI$  solution. It may also be separated from lead by precipitation as the iodide and treatment with  $Na_2S_2O_3$  solution, in which  $PbI_2$  alone is soluble. Useful confirmatory tests are reaction 6 (Section IX, 1A) and the flame test.

Any thallium not precipitated in Group I as  $TlCl$ , will ultimately be found in the precipitate of Group IIIB. It is best to dissolve the Group IIIB precipitate in dilute nitric acid, boil to expel  $H_2S$ , add a few drops of sulphurous acid and boil to expel excess of  $SO_2$ .

The resulting solution is then poured into excess of sodium carbonate solution when the carbonates of cobalt, nickel, manganese and zinc are precipitated. The thallium remains in solution as thallous carbonate and can be precipitated as thallous sulphide  $Tl_2S$  by the addition of ammonium sulphide solution.

#### TUNGSTEN, W

Tungsten forms an unstable dioxide  $WO_2$ , and a stable, yellow acidic oxide  $WO_3$ . The latter oxide is almost insoluble in water and in dilute acids, but is soluble in solutions of (best in fused) caustic alkalis forming tungstates. The latter are the most important compounds of tungsten.

Tungstates form complex acids with phosphoric, boric and silicic acids; tungstic acid cannot therefore be precipitated from these compounds by hydrochloric acid. The complexes may usually be decomposed by heating with concentrated sulphuric acid, tungstic acid being liberated.

### IX, 2. REACTIONS OF TUNGSTATES

Use a solution of sodium tungstate,  $Na_2WO_4 \cdot 2H_2O$ .

**1. Dilute Hydrochloric Acid:** white precipitate of hydrated tungstic acid  $H_2WO_4 \cdot H_2O$  in the cold; upon boiling the mixture, this is converted into yellow tungstic acid  $H_2WO_4$ , insoluble in dilute acids. Similar results are obtained with dilute nitric and sulphuric acids, but not with phosphoric acid. Tartrates, citrates and oxalates inhibit the precipitation of tungstic acid. The ppt. is soluble in dilute ammonia solution (distinction from  $SiO_2 \cdot xH_2O$ ).

**2. Phosphoric Acid:** white precipitate of phosphotungstic acid  $H_3[PO_4(W_{12}O_{36})] \cdot 5H_2O$ , soluble in excess of the reagent.

**3. Hydrogen Sulphide:** no precipitate in acid solution.

**4. Ammonium Sulphide Solution:** no precipitate, but if the solution is afterwards acidified with dilute hydrochloric acid, a brown precipitate of tungsten trisulphide  $WS_3$  is produced. The precipitate dissolves in ammonium sulphide solution forming a thiotungstate  $(NH_4)_2[WS_4]$ .

**5. Zinc and Hydrochloric Acid.**—If a solution of a tungstate is treated with hydrochloric acid and then a little zinc added, a blue coloration or precipitate is produced; this is probably due to  $W_2O_5$  or to  $WCl_5$ .

**6. Stannous Chloride Solution:** yellow precipitate, which becomes blue upon warming with concentrated hydrochloric acid.

† The spot-test technique is as follows. Mix 1–2 drops of the test solution with 3–5 drops of the stannous chloride reagent on a spot plate. A blue precipitate or coloration appears. This is probably due to a lower tungsten oxide ( $W_2O_5$ ).

Sensitivity: 5  $\mu g$ . W. Concentration limit: 1 in 10,000.

Molybdenum gives a similar reaction. If, however, a thiocyanate is added, the red complex ion  $[Mo(SCN)_6]^{3-}$  is formed, and upon the addition of concentrated hydrochloric acid the red colour disappears and the blue colour due to tungsten remains.



The spot test is conducted as follows in the presence of molybdenum:

Place a drop of concentrated hydrochloric acid upon filter or drop-reaction paper and a drop of the test solution in the centre of the spot. A tungstate produces a yellow stain. Add a drop of 10 per cent potassium thiocyanate solution and a drop of the stannous chloride reagent: a red spot, due to  $[\text{Mo}(\text{SCN})_6]^{---}$ , is produced, but this disappears when a drop of concentrated hydrochloric acid is added and a blue colour, due to  $\text{W}_2\text{O}_6$  (?), remains.

Sensitivity: 4  $\mu\text{g}$ . W. Concentration limit: 1 in 12,000.

The reagent consists of a 25 per cent solution of stannous chloride in concentrated hydrochloric acid.

**7. Ferrous Sulphate Solution:** brown precipitate. This turns white upon adding dilute hydrochloric acid, and then yellow upon heating (difference from molybdates).

**8. Silver Nitrate Solution:** pale yellow precipitate of silver tungstate, soluble in ammonia solution, decomposed by nitric acid with the formation of white hydrated tungstic acid.

**9.  $\text{KHSO}_4\text{--H}_2\text{SO}_4\text{--Phenol}$  Test (Defacqz Reaction).—**A little of the solid (or the residue obtained by evaporating a little of the solution to dryness) is heated with 4–5 times the weight of potassium hydrogen sulphate slowly to fusion, and the temperature is maintained until the fluid melt is clear. The cold melt is stirred with concentrated sulphuric acid. Upon adding a few mg. of phenol to a few drops of the sulphuric acid solution, an intense red coloration is produced (difference from molybdate). A reddish-violet coloration is obtained if hydroquinone replaces the phenol. The test is a highly sensitive one and will detect 2  $\mu\text{g}$ . of tungstate.

† Heat a few mg. of the solid unknown with 10–20 mg. of potassium bisulphate and 2 drops of concentrated sulphuric acid in a small porcelain crucible, allow to cool, and add a few mg. of solid phenol. A red coloration is produced.

## Dry Test

*Microcosmic salt bead:* oxidising flame—colourless or pale-yellow; reducing flame—blue, changing to blood-red upon the addition of a little ferrous sulphate.

**Separation.**—Tungsten is precipitated in Group I and is associated with Ag in the ammoniacal filtrate of the group separation. The filtrate is almost neutralised with dilute HCl (any precipitate formed being kept in solution by the addition of ammonia solution), and the silver precipitated as AgI by the addition of KI solution. The filtrate is concentrated, acidified with dilute HCl and reactions 5, 6 or 9 applied.

The following table contains a scheme for the identification of thallos thallium and tungsten (as tungstate) in the presence of lead, mercurous mercury and silver.

## IX, 3. Table I.—Analysis of Group I (Silver Group) in the presence of Tl and W\*

The precipitate may contain  $\text{PbCl}_2$ ,  $\text{AgCl}$ ,  $\text{Hg}_2\text{Cl}_2$ ,  $\text{TlCl}$  and tungstic acid ( $\text{WO}_3 \cdot n\text{H}_2\text{O}$ ). Wash the ppt. on the filter with 2 ml. portions of 2N  $\text{HCl}$ , then 2–3 times with 1 ml. portions of cold water, and reject the washings. Transfer the ppt.† to a boiling tube or to a small beaker, and boil with 10–15 ml. of water. Filter hot.

**Residue.** May contain  $\text{Hg}_2\text{Cl}_2$ ,  $\text{AgCl}$  and tungstic acid. Wash the ppt. several times with hot water until the washings give no ppt. with  $\text{K}_2\text{CrO}_4$  solution; this ensures the complete removal of the Pb and Tl.

Pour 5 ml. of warm, dilute  $\text{NH}_3$  solution repeatedly through the filter.

**Filtrate.** May contain  $\text{PbCl}_2$  and  $\text{TlCl}$ ; these may crystallise out on cooling.

Evaporate to fuming with 2–3 ml. of concentrated  $\text{H}_2\text{SO}_4$ , cool, dilute to 10–20 ml., cool and filter.

**Residue.** If black, consists of  $\text{Hg}(\text{NH}_2)\text{Cl} + \text{Hg}$ .  $\text{Hg}$  (ous) present.

**Filtrate.** May contain  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$  and ammonium tungstate. Nearly neutralise with dilute  $\text{HCl}$ , add just enough dilute  $\text{NH}_3$  solution to redissolve any ppt. which forms. Add  $\text{KI}$  solution and filter.

**Residue.** Pale yellow ( $\text{AgI}$ ).  $\text{Ag}$  present.

**Filtrate.** May contain a tungstate. Evaporate to a small volume, acidify with dilute  $\text{HCl}$ , add 3 ml. of  $\text{SnCl}_2$  solution, boil, add 3 ml. of concentrated  $\text{HCl}$ , and heat again to boiling.

Blue ppt. or coloration.

**W present.**

Confirm by the Defacqz reaction.

**Residue.** If white—consists of  $\text{PbSO}_4$ . This is soluble in ammonium acetate solution;  $\text{K}_2\text{CrO}_4$  solution then precipitates yellow  $\text{PbCrO}_4$ , insoluble in 2N acetic acid.

**Pb present.**

**Filtrate.** May contain  $\text{Tl}_2\text{SO}_4$ . Just neutralise with dilute  $\text{NH}_3$  solution, and add  $\text{KI}$  solution. Yellow ppt. of  $\text{TlI}$ , insoluble in cold  $\text{Na}_2\text{S}_2\text{O}_3$  solution.

**Tl present.** Confirm by flame test; intense green flame. (Use spectroscope, if available.)

## MOLYBDENUM, Mo

Molybdenum forms three basic oxides  $\text{MoO}$ ,  $\text{Mo}_2\text{O}_3$  and  $\text{MoO}_2$ , and one acidic oxide  $\text{MoO}_3$ . The last-named is the most important; it is sparingly soluble in water, but dissolves readily in solutions of alkalis forming molybdates.

\* Compare Table III, Section VII, 8.

† A gelatinous precipitate may also be hydrated silica, which is partially precipitated here from silicates decomposable by acids.

## IX, 4. REACTIONS OF MOLYBDATES

Use a solution of ammonium molybdate  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ .

1. **Dilute Hydrochloric Acid:** white or yellow precipitate of molybdic acid  $\text{H}_2\text{MoO}_4$  from concentrated solutions, soluble in excess of mineral acid.

2. **Hydrogen Sulphide.**—With a small quantity of the gas and an acidified molybdate solution, a blue coloration is produced; further passage of hydrogen sulphide yields a brown precipitate of the trisulphide  $\text{MoS}_3$ , soluble in ammonium sulphide solution to a solution containing a thiomolybdate  $(\text{NH}_4)_2[\text{MoS}_4]$ , from which  $\text{MoS}_3$  is reprecipitated by the addition of acids. The precipitation in acid solution is incomplete in the cold; more extensive precipitation is obtained by the prolonged passage of the gas into the boiling solution and under pressure. Precipitation is quantitative with excess of hydrogen sulphide at  $0^\circ$  in the presence of formic acid.

3. **Reducing Agents, e.g. zinc, stannous chloride solution:** colour a molybdate solution acidified with dilute hydrochloric acid blue (probably due to  $\text{MoCl}_3$ ), then green and finally brown.

4. **Ammonium Thiocyanate Solution:** yellow coloration in solution acidified with dilute hydrochloric acid, becoming blood-red upon the addition of zinc or of stannous chloride on account of the formation of ammonium molybdo-thiocyanate  $(\text{NH}_4)_3[\text{Mo}(\text{CNS})_6]$ ; the latter is soluble in ether. The red coloration is produced in the presence of phosphoric acid (difference from iron).

† The spot-test technique is as follows. Place a drop of the test solution and a drop of 10 per cent potassium or ammonium thiocyanate solution upon quantitative filter paper or upon drop-reaction paper. Add a drop of stannous chloride solution (5 per cent in 3N HCl). A red spot is obtained.

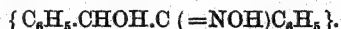
Sensitivity: 0.1  $\mu\text{g. Mo}$ . Concentration limit: 1 in 500,000.

If iron is present, a red spot will appear initially but this disappears upon the addition of the stannous chloride solution (or of sodium thiosulphate solution). Tungstates reduce the sensitivity of the test (compare Section IX, 2, reaction 6).

5. **Sodium Phosphate Solution:** yellow, crystalline precipitate of ammonium phosphomolybdate in the presence of excess of nitric acid (compare Phosphates, Section IV, 28, reaction 4).

6. **Potassium Ferrocyanide Solution:** reddish-brown precipitate of molybdenum ferrocyanide, insoluble in dilute mineral acids, but readily soluble in solutions of caustic alkalis and ammonia (difference from uranyl and cupric ferrocyanides).

7.  **$\alpha$ -Benzoin Oxime Reagent (or "Cupron" Reagent)**



The molybdate solution is strongly acidified with dilute sulphuric

acid and 0.5 ml. of the reagent added. A white precipitate is produced.

**8. Potassium Xanthate (or Potassium Ethyl Xanthogenate)**

**Test**  $\{\text{SC}(\text{SK})\text{OC}_2\text{H}_5\}$ .—When a molybdate solution is treated with a little solid potassium xanthate and then acidified with dilute hydrochloric acid, a red-purple coloration is produced. With large amounts of molybdenum, the compound separates as dark oily drops which are readily soluble in organic solvents such as benzene, chloroform and carbon disulphide. The reaction product has been given the formula  $\text{MoO}_2[\text{SC}(\text{SH})(\text{OC}_2\text{H}_5)]_2$ . The test is said to be specific for molybdates, although copper, cobalt, nickel, iron, chromium and uranium under exceptional conditions interfere. Large quantities of oxalates, tartrates and citrates decrease the sensitivity of the test.

† The spot-test technique, for which the reaction is particularly well adapted, is as follows. Place a drop of the nearly neutral or faintly acid test solution on a spot plate, introduce a minute crystal of potassium xanthate, followed by 2 drops of 2N hydrochloric acid. An intense red-violet coloration is obtained.

Sensitivity: 0.04  $\mu\text{g}$ . Mo. Concentration limit: 1 in 250,000.

† **9. Phenylhydrazine Reagent** ( $\text{C}_6\text{H}_5\cdot\text{NHNH}_2$ ).—A red coloration or precipitate is produced when molybdates and an acid solution of phenylhydrazine react. The latter is oxidised by the molybdate to a diazonium salt, which then couples with the excess of base in the presence of the molybdate to yield a coloured compound.

Mix a drop of the test solution and a drop of the reagent on a spot plate. A red coloration appears.

Sensitivity: 0.3  $\mu\text{g}$ . Mo. Concentration limit: 1 in 150,000.

Alternatively, place a drop of the reagent on drop-reaction paper and immediately add a drop of the test solution. A red ring forms round the spot.

Se, Te, Sb (III), Sn (IV), tungstate, vanadate and oxalate interfere.

Sensitivity: 0.1  $\mu\text{g}$ . Mo. Concentration limit: 1 in 300,000.

The reagent consists of a solution of 1 part of phenylhydrazine dissolved in 2 parts of glacial acetic acid.

**10. Ferrous Sulphate Solution:** reddish-brown colour. Upon adding dilute mineral acid, the colour changes to blue; the colour becomes paler and more green upon warming but returns to blue on cooling (difference from tungstate).

**Dry Tests**

(i) *Microcosmic salt bead*: oxidising flame—yellow to green while hot and colourless when cold; reducing flame—brown when hot, green when cold.

(ii) Upon evaporation with concentrated sulphuric acid in a porcelain dish or crucible, a blue mass (containing "molybdenum

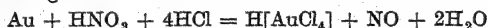
blue") is obtained. The blue colour is destroyed by dilution with water.

**Separation.**—Molybdenum appears along with As, Sb, Sn, Au and Pt in the ordinary process of analysis. Upon acidification of the yellow ammonium sulphide solution extract and boiling with concentrated HCl,  $\text{MoS}_3$  appears with the  $\text{As}_2\text{S}_3$ . The mixture of  $\text{MoS}_3$  and  $\text{As}_2\text{S}_3$  is dissolved in  $\text{HNO}_3$ , the As removed with the magnesium nitrate reagent or with magnesia mixture and the Mo detected in the filtrate by test 4 or 8 or the dry test (ii).

See also Table IV in Section IX, 10.

#### GOLD, Au

Gold is a very stable metal. It is unattacked by mineral acids, but dissolves readily in aqua regia:



The metal is also soluble *inter alia* in chlorine and bromine water forming respectively  $\text{AuCl}_3$  and  $\text{AuBr}_3$ ; these combine with potassium chloride and potassium bromide to produce the crystalline aurichloride  $\text{K}[\text{AuCl}_4]$  and auribromide  $\text{K}[\text{AuBr}_4]$  respectively. The commercial metal is usually alloyed with copper and/or silver.

Two oxides  $\text{Au}_2\text{O}$  and  $\text{Au}_2\text{O}_3$  are known; these correspond to the aurous and auric salts respectively. The latter are the more stable and exhibit a marked tendency to form complex salts of the type  $\text{R}[\text{AuX}_4]$ .

### IX, 5. REACTIONS OF AURIC COMPOUNDS

Use a solution of gold chloride (hydrogen aurichloride or aurichloric acid),  $\text{H}[\text{AuCl}_4] \cdot 3\text{H}_2\text{O}$ .

**1. Hydrogen Sulphide:** black precipitate of aurous sulphide  $\text{Au}_2\text{S}$  (usually mixed with a little free gold) in the cold, insoluble in dilute acids, but largely soluble in yellow ammonium sulphide solution, from which it is reprecipitated by dilute hydrochloric acid. A brown precipitate of metallic gold, together with aurous sulphide and sulphur, is obtained upon precipitation of a hot solution; this is also largely dissolved by yellow ammonium sulphide solution.



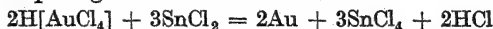
**2. Ammonia Solution:** yellow precipitate of "fulminating gold"; this has been formulated as  $\text{Au}_2\text{O}_3 \cdot 3\text{NH}_3 + \text{NH}(\text{ClNH}_2\text{Au})_2$  but the exact composition is not fully established. The dry substance explodes upon heating or upon percussion.

**3. Oxalic Acid Solution.**—Gold is precipitated as a fine brown powder (or sometimes as a mirror) from cold neutral solutions (difference from platinum and other Group II metals). Under suitable conditions, the gold is obtained in the colloidal state as a red, violet or blue solution.

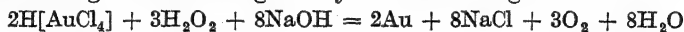


Similar results are obtained with ferrous sulphate solution. Reduction also occurs with hydroxylamine and hydrazine salts.

**4. Stannous Chloride Solution:** purple precipitate, "purple of Cassius," consisting of an adsorption compound of stannous hydroxide  $\text{Sn}(\text{OH})_2$  and colloidal gold, in neutral or weakly acid solution. In extremely dilute solutions, only a purple coloration is produced. If the solution is strongly acid with hydrochloric acid, a dark-brown precipitate of pure gold is formed.



**5. Hydrogen Peroxide:** the finely divided metal is precipitated in the presence of sodium hydroxide solution (distinction from platinum). The precipitated metal appears brownish-black by reflected light and bluish-green by transmitted light.



**6. Sodium Hydroxide Solution:** reddish-brown precipitate of auric hydroxide  $\text{Au}(\text{OH})_3$  from *concentrated* solutions. The precipitate has amphoteric properties; it dissolves in excess of alkali forming aurates containing the  $[\text{AuO}_2]^-$  ion.

† **7. para - Dimethylamino - benzylidene - rhodanine Reagent\*:** red-violet precipitate in neutral or faintly acid solution. Silver, mercury and palladium salts give coloured compounds with the reagent and must therefore be absent.

Moisten a piece of drop-reaction paper with the reagent and dry it. Place a drop of the neutral or weakly acid test solution upon it. A violet spot or ring is obtained.

Sensitivity: 0.1  $\mu\text{g}$ . Au. Concentration limit: 1 in 500,000.

The reagent consists of a 0.03 per cent solution of *p*-dimethylamino-benzylidene-rhodanine in acetone.

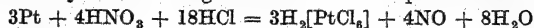
### Dry Test

All gold compounds when heated upon charcoal with sodium carbonate yield yellow, malleable, metallic particles, which are insoluble in nitric acid, but soluble in aqua regia. The aqua regia solution should be evaporated to dryness, dissolved in water and tests 1, 3 or 4 applied.

**Separation.**—Gold is usually detected and determined by dry methods. In the wet way, it is precipitated by  $\text{H}_2\text{S}$  in Group II, dissolved by yellow ammonium sulphide solution and reprecipitated from the latter by concentrated  $\text{HCl}$  along with  $\text{As}_2\text{S}_3$  and  $\text{MoS}_3$ . Separation from  $\text{As}_2\text{S}_3$  and  $\text{MoS}_3$  is effected by concentrated  $\text{HNO}_3$ , in which the gold precipitate is insoluble. The gold may then be dissolved in aqua regia and identified by reactions 1, 3 or 4. See also Table II in Section IX, 10.

### PLATINUM, Pt

Platinum, like gold, is unattacked by mineral acids; it dissolves in *aqua regia* to form a yellowish-orange solution of chloroplatinic acid  $\text{H}_2[\text{PtCl}_6]$ :



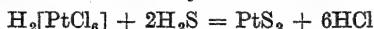
This acid and its salts are the most commonly occurring platinum compounds.

\* For formula, see under Silver, Section III, 4, reaction 7.

## IX, 6. REACTIONS OF CHLOROPLATINATES

Use a solution of chloroplatinic acid,  $\text{H}_2[\text{PtCl}_6] \cdot 6\text{H}_2\text{O}$ .\*

1. **Hydrogen Sulphide:** black (or dark brown) precipitate of the disulphide  $\text{PtS}_2$  (possibly containing a little elementary platinum), slowly formed in the cold, but rapidly on warming. The precipitate is insoluble in concentrated acids, but dissolves in aqua regia and also in yellow ammonium sulphide solution; it is reprecipitated from the last-named solution of thio salt by dilute acids.



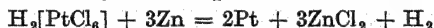
2. **Potassium Chloride Solution:** yellow precipitate of potassium chloroplatinate  $\text{K}_2[\text{PtCl}_6]$  from concentrated solutions (difference from gold). A similar result is obtained with ammonium chloride solution.

3. **Oxalic Acid Solution:** no precipitate of platinum (difference from gold). Hydrogen peroxide and sodium hydroxide solution likewise do not precipitate metallic platinum.

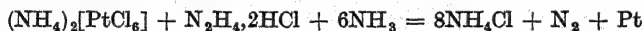
4. **Formic Acid:** black powder of metallic platinum from neutral boiling solutions.



5. **Zinc, Cadmium, Magnesium or Aluminium:** all these metals precipitate finely divided platinum.



6. **Hydrazine Hydrochloride:** ready reduction in ammoniacal solution to metallic platinum, some of which is deposited as a mirror upon the sides of the tube.



7. **Silver Nitrate Solution:** yellow precipitate of silver chloroplatinate  $\text{Ag}_2[\text{PtCl}_6]$ , sparingly soluble in ammonia solution but soluble in solutions of alkali cyanides and of alkali thiosulphates.

8. **Potassium Iodide Solution:** intense brownish-red or red coloration, due to  $[\text{PtI}_6]^-$  ions. With excess of the reagent  $\text{K}_2[\text{PtI}_6]$  may be precipitated as an unstable brown solid. On warming, black  $\text{PtI}_4$  may be precipitated.

9. **Stannous Chloride Solution:** red or yellow coloration, due to colloidal platinum, soluble in ethyl acetate or in ether.

† To employ this reaction as a spot test in the presence of other noble metals (gold, palladium, etc.), the platinum is fixed as thallos chloroplatinate  $\text{TI}_3[\text{PtCl}_6]$ , which is stable to ammonia solution; upon washing the precipitate with ammonia solution, the thallium complexes with gold, palladium, etc., pass into solution.

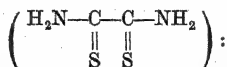
Place a drop of saturated thallos nitrate solution upon drop-reaction paper, add a drop of the test solution and then another drop of the

\* Commonly called "platinic chloride."

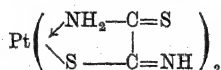
thallous nitrate solution. Wash the precipitate with ammonia solution, and add a drop of strongly acid stannous chloride solution. A yellow or orange spot remains.

Sensitivity: 0.5  $\mu$ g. Pt. Concentration limit: 1 in 80,000.

†10. **Rubeanic Acid (or Dithio-oxamide) Reagent**



a purplish-red precipitate of the complex



is formed. Palladium and a large proportion of gold interfere.

Place a drop of the test solution (acid with HCl) upon a spot plate and add a drop of the reagent. A purplish-red precipitate is produced.

Concentration limit: 1 in 10,000.

The reagent consists of a 0.02 per cent solution of rubeanic acid in glacial acetic acid.

### Dry Test

All platinum compounds when fused with sodium carbonate upon charcoal are reduced to the grey, spongy metal (distinction from gold). The residue is insoluble in concentrated mineral acids, but dissolves in aqua regia. The solution is evaporated almost to dryness, dissolved in water and reactions 1, 2, 5, 9 or 10 applied.

**Separation.**—Platinum is precipitated in Group II as  $\text{PtS}_2$ . The Group IIB metals are extracted with yellow ammonium sulphide solution and reprecipitated with HCl. The sulphides of As, Sb, Sn, Au, Pt and Mo are dissolved in aqua regia, the excess of acid evaporated and  $\text{NH}_4\text{Cl}$  solution added. A yellow precipitate of  $(\text{NH}_4)_2[\text{PtCl}_6]$  indicates the presence of Pt. The filtrate is treated with  $\text{FeSO}_4$  solution; Au is precipitated and is removed. The filtrate is again treated with  $\text{H}_2\text{S}$  to reprecipitate As, Sb, Sn and Mo as sulphides, which are filtered off. These sulphides are then separated as described under Molybdates (Section IX, 4).

See also Table II in Section IX, 10.

### PALLADIUM, Pd

Palladium, unlike platinum, is slowly dissolved by concentrated nitric acid {forming a brown solution of palladous nitrate,  $\text{Pd}(\text{NO}_3)_2$ }, and by hot concentrated sulphuric acid (forming palladous sulphate,  $\text{PdSO}_4$ ; the latter is readily produced by fusing with potassium pyrosulphate). The metal dissolves readily in aqua regia yielding a mixture of palladous and palladic chlorides or, more probably, the complex acids  $\text{H}_2[\text{PdCl}_4]$  and  $\text{H}_2[\text{PdCl}_6]$ ; upon evaporation to dryness, the latter loses chlorine so that on treating the residue with water a solution of palladous chloride or of chloropalladous acid  $\text{H}_2[\text{PdCl}_4]$  is obtained.



Palladium forms two oxides,  $\text{PdO}$  and  $\text{PdO}_2$ : palladous compounds may be regarded as derived from the former and palladic compounds from the latter. The palladous compounds are by far the more stable and their reactions will be studied.

## IX. 7. REACTIONS OF PALLADOUS COMPOUNDS

Use a solution of palladous chloride,  $\text{PdCl}_2$ .

**1. Hydrogen Sulphide:** black precipitate of palladous sulphide  $\text{PdS}$  from acid or neutral solutions. The precipitate is insoluble in ammonium sulphide solution.

**2. Sodium Hydroxide Solution:** reddish-brown, gelatinous precipitate of the hydrated oxide  $\text{PdO} \cdot n\text{H}_2\text{O}$  (this may be contaminated with a basic salt), soluble in excess of the precipitant.

**3. Ammonia Solution:** red precipitate of  $[\text{Pd}(\text{NH}_3)_4][\text{PdCl}_4]$ , soluble in excess of the reagent to give a colourless solution of  $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ . Upon acidifying the latter solution with hydrochloric acid, a yellow crystalline precipitate of  $[\text{Pd}(\text{NH}_3)_2\text{Cl}_2]$  is obtained.

**4. Potassium Iodide Solution:** black precipitate of palladous iodide  $\text{PdI}_2$  in neutral solution, soluble in excess of the reagent to give a brown solution of  $\text{K}_2[\text{PdI}_4]$ . In acid solution, black  $\text{PdI}_2$  is precipitated.

**5. Mercuric Cyanide Solution:** white precipitate of palladous cyanide  $\text{Pd}(\text{CN})_2$  (difference from platinum), difficultly soluble in dilute hydrochloric acid, readily soluble in potassium cyanide solution and in ammonia solution.

**6.  $\alpha$ -Nitroso- $\beta$ -naphthol Solution:** brown, voluminous precipitate of  $\text{Pd}(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_2$  (difference from platinum).

The reagent consists of a cold, saturated solution of  $\alpha$ -nitroso- $\beta$ -naphthol in 50 per cent acetic acid.

**7. Reducing Agents** ( $\text{Cd}$ ,  $\text{Zn}$  or  $\text{Fe}$  in acid solution, formic acid, sulphurous acid, etc.): black, spongy precipitate of metallic palladium, "palladium black." Stannous chloride yields a brown suspension containing metallic palladium.

**8. Dimethylglyoxime Reagent:** yellow, crystalline precipitate of palladium dimethylglyoxime  $\text{Pd}(\text{C}_4\text{H}_7\text{O}_2\text{N}_2)_2$ , insoluble in *N* hydrochloric acid (difference from nickel and from other platinum metals) but soluble in dilute ammonia solution and in potassium cyanide solution (compare Nickel, Section III, 25, reaction 8).

Salicylaldoxime reagent also precipitates palladium quantitatively as  $\text{Pd}(\text{C}_7\text{H}_6\text{O}_2\text{N})_2$  (compare Section III, 8, reaction 10) (difference from platinum).

† Place a drop of the slightly acid solution on a microscope slide and add a minute crystal of dimethylglyoxime. After some minutes, a yellow precipitate is formed. This consists of long, very characteristic needles when examined under a microscope ( $\times 75$ ).

Platinum does not interfere, but gold and nickel give a similar reaction.

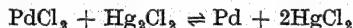
Concentration limit: 1 in 10,000.

A useful spot test utilises the fact that a suspension of red nickel dimethylglyoxime in water when treated with a neutral or acetic acid solution of a palladium salt yields the yellow palladium dimethylglyoxime, which is sparingly soluble in dilute acids. The test is best performed with dimethylglyoxime paper: the latter is prepared as follows. Immerse drop-reaction paper in a cold, saturated alcoholic solution of dimethylglyoxime, dry, then immerse again in a solution of 2*N* nickel nitrate rendered barely ammoniacal: the nickel complex precipitates; wash thoroughly with water, immerse in alcohol and dry.

Place a drop of the neutral or acetic acid test solution upon nickel dimethylglyoxime paper, and almost dry by waving over a flame. Immerse the paper in dilute hydrochloric acid until the surface surrounding the fleck becomes white, and then wash the paper with cold water. A pink to red spot remains, depending upon the quantity of palladium present. The acid-stable palladium dimethylglyoxime at the site of the fleck protects the underlying red nickel dimethylglyoxime from attack by the acid.

Sensitivity: 0.05  $\mu$ g. Pd. Concentration limit: 1 in 1,000,000.

#### 9. Mercurous Chloride: reduced to metallic palladium.



Shake the slightly acid test solution with solid mercurous chloride in the cold. The solid acquires a grey colour.

Concentration limit: 1 in 100,000.

**Separation.** Palladium is precipitated in Group II as PdS; it is insoluble in yellow ammonium sulphide solution and therefore accompanies the elements of Group IIA. It is ultimately identified in acid solution as the dimethylglyoxime complex.

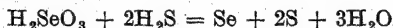
#### SELENIUM, Se

Selenium resembles sulphur in many of its properties. It is converted by nitric acid or by aqua regia into selenium dioxide  $\text{SeO}_2$  (or selenious acid  $\text{H}_2\text{SeO}_3$ ). In analytical work the element is most frequently encountered in the form of selenites  $\text{R}_2\text{SeO}_3$  and as the less stable selenates  $\text{R}_2\text{SeO}_4$ .

#### IX, 8A. REACTIONS OF SELENITES

Use a solution of selenious acid,  $\text{H}_2\text{SeO}_3$ ,\* or of sodium selenite,  $\text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O}$ .

**1. Hydrogen Sulphide:** yellow precipitate, consisting of a mixture of selenium and sulphur, in the cold, becoming red on heating. The precipitate is readily soluble in yellow ammonium sulphide solution.



**2. Reducing Agents** {sulphur dioxide, solution of stannous chloride, ferrous sulphate, hydroxylamine hydrochloride, hydrazine

\* Also produced by dissolving selenium dioxide  $\text{SeO}_2$  in water.

hydrochloride or hydriodic acid ( $KI + HCl$ ), zinc or iron}: red precipitate of selenium in hydrochloric acid solution. The precipitate frequently turns greyish-black on warming. When solutions in concentrated hydrochloric acid are boiled or evaporated, serious losses of selenium as  $SeCl_4$  occur.

**3. Copper Sulphate Solution:** bluish-green, crystalline precipitate of copper selenite  $CuSeO_3$  in neutral solution (difference from selenate). The precipitate is soluble in dilute acetic acid.

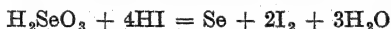
**4. Barium Chloride Solution:** white precipitate of barium selenite  $BaSeO_3$  in neutral solution, soluble in dilute mineral acids.

†**5. Thiourea Test**  $\{CS(NH_2)_2\}$ .—Solid or dissolved thiourea precipitates selenium as a red powder from cold dilute solutions of selenites. Tellurium and bismuth give yellow precipitates, whilst large amounts of nitrite and of copper interfere.

Place a little powdered thiourea on quantitative filter paper and moisten it with a drop of the test solution. Orange-red selenium separates out.

Sensitivity: 2  $\mu g.$  Se.

†**6. Hydriodic Acid Test.**—Selenites are reduced by hydriodic acid (or by potassium iodide and hydrochloric acid):

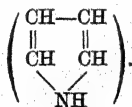


The iodine is removed by adding a thiosulphate, and the selenium remains as a reddish-brown powder. Tellurites react under these conditions forming the complex anion  $[TeI_6]^-$ , which also has a reddish brown colour; it is, however, decomposed and decolourised by a thio-sulphate, thus permitting the detection of selenium in the presence of not too large an excess of tellurium.

Place a drop of concentrated hydriodic acid (or a drop each of concentrated potassium iodide solution and of concentrated hydrochloric acid) upon drop-reaction paper and introduce a drop of the acid test solution into the middle of the original drop. A brownish-black spot appears. Add a drop of 5 per cent sodium thiosulphate solution to the spot; a reddish-brown stain of elementary selenium remains.

Sensitivity: 1  $\mu g.$  Se (in 0.025 ml.). Concentration limit: 1 in 25,000.

#### † 7. Pyrrole Reagent



Selenious acid oxidises pyrrole to a blue dyestuff of unknown composition ("pyrrole blue"). Iron salts accelerate the reaction when it is carried out in phosphoric acid solution. Selenic, tellurous and telluric acids do not react under the conditions given below: the test therefore provides a method of distinguishing selenites and selenates.

Place a drop of 5 per cent ferric chloride solution and 7 drops of syrupy phosphoric acid (sp. gr. 1.75) on a spot plate containing 1 drop

of the test solution and stir well. Add a drop of the pyrrole reagent and stir again. A greenish-blue coloration is obtained.

Sensitivity: 0.5  $\mu$ g. Se. Concentration limit: 1 in 100,000.

The reagent consists of a 1 per cent solution of pyrrole in aldehyde-free ethyl alcohol.

**8. Ammonium Thiocyanate and Hydrochloric Acid.**—Selenites are reduced in acid solution to elementary selenium:



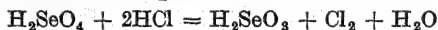
Mix 0.5 ml. of the test solution with 2 ml. of saturated ammonium thiocyanate solution and 5 ml. of 6*N* hydrochloric acid, and boil for 30 seconds. A red coloration, due to selenium, is produced.

This sensitive test may be adapted to the semimicro scale: the concentration limit is 1 part in 100,000. The following interfere: arsenic (III), antimony (III), iron (II) and molybdates.

## IX, 8B. REACTIONS OF SELENATES

Use a solution of potassium selenate,  $\text{K}_2\text{SeO}_4$  or of sodium selenate,  $\text{Na}_2\text{SeO}_4 \cdot 10\text{H}_2\text{O}$ .

**1. Hydrogen Sulphide:** no precipitation occurs. If the solution is boiled with concentrated hydrochloric acid, the selenic acid is reduced to selenious acid; hydrogen sulphide then precipitates a mixture of selenium and sulphur.



**2. Sulphur Dioxide:** no reducing action.

**3. Copper Sulphate Solution:** no precipitate (difference from selenite).

**4. Barium Chloride Solution:** white precipitate of barium selenate  $\text{BaSeO}_4$ , insoluble in dilute mineral acids. The precipitate dissolves when boiled with concentrated hydrochloric acid, and chlorine is evolved (distinction and separation from sulphate).



### Dry Tests

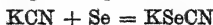
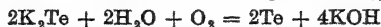
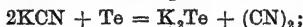
(i) All selenium compounds when mixed with sodium carbonate and heated upon charcoal emit the odour of rotten horseradish. A foul odour, due to hydrogen selenide  $\text{H}_2\text{Se}$ , is obtained upon moistening the residue with a few drops of dilute hydrochloric acid. A black stain (due to  $\text{Ag}_2\text{Se}$ ) is produced when the moistened residue is placed in contact with a silver coin.

(ii) Elementary selenium dissolves in concentrated sulphuric acid to yield a green solution, due to the presence of the compound  $\text{SSeO}_3$ . Upon dilution with water, red selenium is precipitated.

**Separation.**—See under tellurium (Section IX, 9).

## TELLURIUM, Te

Tellurium is less widely distributed in nature than selenium; both elements belong to Group VI of the periodic system. When fused with potassium cyanide, it is converted into potassium telluride  $K_2Te$ , which dissolves in water to yield a red solution. If air is passed through the solution, the tellurium is precipitated as a black powder (difference and method of separation from selenium). Selenium under similar conditions yields the stable potassium selenocyanide  $KSeCN$ ; the selenium may be precipitated by the addition of dilute hydrochloric acid to its aqueous solution.



Tellurium is converted into the dioxide  $TeO_2$  by nitric acid. Like sulphur and selenium, it forms two series of salts, the tellurites  $R_2TeO_3$  and the tellurates  $R_2TeO_4$ .

## IX, 9A.

## REACTIONS OF TELLURITES

Use a solution of sodium or potassium tellurite,  $Na_2TeO_3$  or  $K_2TeO_3$ .

1. **Hydrogen Sulphide:** brown precipitate of the disulphide  $TeS_2$  from acid solutions. The sulphide decomposes easily into tellurium and sulphur, and is readily soluble in ammonium sulphide solution but insoluble in concentrated hydrochloric acid.

2. **Sulphur Dioxide:** complete precipitation of tellurium from dilute (1-5*N*) hydrochloric acid solutions as a black powder. In the presence of much concentrated hydrochloric acid, no precipitate is formed (difference and method of separation from selenium).

3. **Ferrous Sulphate Solution:** no precipitation of tellurium (difference from selenium). A similar result is obtained with hydriodic acid ( $KI + HCl$ ).

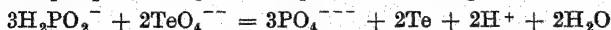
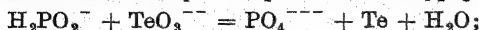
4. **Stannous Chloride or Hydrazine Hydrochloride Solution or Zinc:** black tellurium is precipitated.

5. **Dilute Hydrochloric Acid:** white precipitate of tellurous acid  $H_2TeO_3$  (difference from selenite), soluble in excess of the precipitant.

6. **Barium Chloride Solution:** white precipitate of barium tellurite  $BaTeO_3$ , soluble in dilute hydrochloric acid but insoluble in 30 per cent acetic acid.

7. **Potassium Iodide Solution:** black precipitate of  $TeI_4$  in faintly acid solution, dissolving in excess of the reagent to form the red potassium telluri-iodide  $K_2[TeI_6]$  (difference from selenite).

†8. **Hypophosphorous Acid Test.**—Both tellurites and tellurates are reduced to tellurium upon evaporation with hypophosphorous acid:



Selenites are likewise reduced to selenium. If, however, the solution of the selenite in concentrated sulphuric acid is treated with sodium sulphite, selenium separates but the tellurite is unaffected; the latter can be detected in the solution after eliminating the sulphur dioxide. Salts of silver, copper, gold and platinum must be absent for they are reduced to the metal by the reagent.

Mix a drop of the test solution in mineral acid and a drop of 50 per cent hypophosphorous acid in a porcelain microcrucible, and evaporate almost to dryness. Black grains or a grey stain of tellurium are obtained.

Sensitivity: 0.1  $\mu$ g. tellurous acid; concentration limit: 1 in 500,000; 0.5  $\mu$ g. telluric acid; concentration limit: 1 in 100,000.

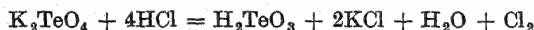
## IX, 9B. REACTIONS OF TELLURATES

Use a solution of potassium tellurate,  $K_2TeO_4$ .

**1. Hydrogen Sulphide:** no precipitate in hydrochloric acid solution in the cold. In hot acid solution, the tellurate is first reduced to tellurite, and precipitation of the tellurium then occurs (compare Section IX, 9A). Other reducing agents give similar results.



**2. Hydrochloric Acid:** no precipitate in the cold. Upon boiling the solution, chlorine is evolved; tellurous acid  $H_2TeO_3$  is thrown down upon dilution (distinction from selenium).



**3. Barium Chloride Solution:** white precipitate of barium tellurate  $BaTeO_4$  from neutral solutions; the precipitate is readily soluble in dilute hydrochloric acid and in dilute acetic acid (distinction from selenate).

**4. Potassium or Sodium Iodide Solution:** yellow to red colour, due to  $[TeI_6]^{--}$ , from dilute acid solutions (difference from tellurites).

**5. Reducing Agents.**—No precipitate is produced in cold solutions with hydrogen sulphide or sulphur dioxide; with hot solutions, or with solutions that have been boiled with hydrochloric acid, precipitates of brown  $TeS$  (or  $Te + S$ ) and of black  $Te$  respectively are formed. Stannous chloride, hydrazine or zinc in acid solution give black tellurium upon warming.

### Dry Tests

(i) Fusion of any tellurium compound with sodium carbonate upon charcoal results in the formation of sodium telluride  $Na_2Te$ , which produces a black stain (due to  $Ag_2Te$ ) when placed in contact with a moist silver coin.

(ii) Elementary tellurium dissolves in concentrated sulphuric acid to yield a red solution, due to the presence of  $\text{STeO}_3$ . Upon dilution with water, grey tellurium is precipitated.

**Separation.**—Selenium and tellurium are precipitated in Group II as the yellow Se-S mixture and brown Te-S mixture respectively. Both dissolve in ammonium sulphide solution and are precipitated with  $\text{As}_2\text{S}_3$  upon the addition of concentrated  $\text{HCl}$ . They may be identified by the  $\text{H}_2\text{SO}_3$  tests.

The following table contains a scheme for the separation of the Group II elements in the presence of Mo, Au, Pt, Pd, Se and Te.

### IX, 10. Table II.—Analysis of Group II (Copper and Arsenic Groups) in the presence of Mo, Au, Pt, Pd, Se and Te\*

Hydrogen sulphide in acid solution precipitates Mo,† Au, Pt, Pd, Se and Te in addition to the "common" elements of Group II. Extraction of the group precipitate with yellow ammonium sulphide solution brings the greater part of the "rarer" elements (excluding PdS) into Group IIB (arsenic group) but not completely, for appreciable quantities of Mo, Au and Pt, as well as all the Pd, remain in the Group IIA (copper group) precipitate. The latter three elements and also Pd are therefore also tested for in Group IIA.

Transfer the Group II precipitate, which has been well washed with 5%  $\text{NH}_4\text{Cl}$  solution that has been saturated with  $\text{H}_2\text{S}$ , to a porcelain dish, add 5–10 ml. of yellow ammonium sulphide solution, heat to  $50\text{--}60^\circ\text{C}$  and maintain at this temperature for 3–4 minutes with constant stirring. Filter. Wash the precipitate with dilute (1 : 100) ammonium sulphide solution.

**Residue.** May contain  $\text{HgS}$ ,  $\text{PbS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{CuS}$ ,  $\text{CdS}$ ,  $\text{PdS}$  together with Au, Pt, Mo (trace), Sn (trace) as sulphides.

**Group IIA present.**

**Filtrate.** May contain solutions of the thio-salts of As, Sb and Sn together with Mo, Au, Pt, Se and Te. Just acidify by adding concentrated  $\text{HCl}$  drop by drop (test with litmus paper) and warm gently.

A coloured precipitate indicates  
**Group IIB present.**

\* Compare corresponding tables in Section VII, 9 to VII, 11.

† For the almost complete precipitation of Mo in Group II, it has been recommended that the solution be first saturated in the cold with hydrogen sulphide, then transferred to a pressure bottle and heated on a water bath.

Proceed to the analysis of Groups IIA and IIB as detailed below.

**IX, 10. Table III.—Analysis of Group IIA (Copper Group)**

The precipitate may contain  $\text{HgS}$ ,  $\text{PbS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{CuS}$ ,  $\text{CdS}$  and  $\text{PdS}$ , together with  $\text{Au}$  and  $\text{Pt}$  and also  $\text{Mo}$  sulphide (trace). Transfer to a beaker or porcelain dish, add 5–10 ml. of dilute  $\text{HNO}_3$ , boil for 2–5 minutes and filter.

**Residue.** May contain  $\text{HgS}$ ,  $\text{Pt}$  and  $\text{Au}$ . Boil with concentrated  $\text{HCl}$  and a little bromine water, and filter, if necessary, from traces of  $\text{SnO}_2$  and  $\text{PbSO}_4$  which may separate here. Add  $\text{KCl}$  solution and  $\text{HCl}$ , and concentrate the solution. Filter.

**Filtrate.** May contain nitrates of  $\text{Pb}$ ,  $\text{Bi}$ ,  $\text{Cu}$ ,  $\text{Cd}$  and  $\text{Pd}$ .

Examine for  $\text{Pb}$ ,  $\text{Bi}$ ,  $\text{Cu}$  and  $\text{Cd}$  by Table V in Section VII, 10. After separation of  $\text{Cu}$  and  $\text{Cd}$ , acidify the solution with dilute  $\text{HCl}$ , introduce a few zinc granules and after several minutes filter off any solid and wash with water. Dissolve the ppt. in 2 ml. of aqua regia, evaporate just to dryness, dissolve the residue in  $N$   $\text{HCl}$  and add dimethylglyoxime reagent.

Yellow ppt.

**Pd present.**

**Residue.**  
Yellow  
and  
crystalline  
 $\text{K}_2[\text{PtCl}_6]$ .  
**Pt**  
**present.**

**Filtrate.** May contain  $\text{AuCl}_3$  and  $\text{HgCl}_2$ . Boil to remove excess of acid, render alkaline with  $\text{NaOH}$  solution and boil with excess of oxalic acid. Filter.

**Residue.**  
Brownish-  
black or  
purplish-  
black.  
**Au present.**

**Filtrate.** May contain  $\text{HgCl}_2$ . Add a few drops of  $\text{SnCl}_2$  solution. White or grey ppt.\*  
**Hg present.**

\* Alternatively, the ethylenediamine test, Section III, 5, reaction 7, may be applied to the neutral or slightly ammoniacal solution.



## IX, 10. Table IV.—Analysis of Group IIB (Arsenic Group)

Transfer the ppt. to a small conical flask, add 5 ml. of concentrated HCl, and boil gently for 5 minutes (with funnel in mouth of flask). Dilute with 2-3 ml. of water, and filter.			
<b>Residue.</b> May contain As, Au, Pt, Mo, Se and Te as sulphides. Dissolve in concentrated HCl + a little solid $\text{KClO}_3$ ; concentrate the solution to the crystallisation point (use a water bath to reduce loss of Se to a minimum). Filter.		<b>Filtrate.</b> May contain Sb and Sn as chlorides or complex chloro-acids. Examine by Table VI in Section VII, 11.	
<b>Residue.</b> Yellow $\text{K}_2[\text{PtCl}_6]$ . <b>Pt</b> <b>present.</b> Confirm by dissolving in a little hot water and adding KI solution. Red or brownish-red coloration. Alternatively, apply the rubeanic acid test (Section IX, 6, reaction 10).	<b>Filtrate.</b> May contain As, Au, Mo, Se and Te as chlorides or acids. Render alkaline with ammonia solution, add $\text{Mg}(\text{NO}_3)_2$ reagent or magnesia mixture, allow to stand for 5 minutes with frequent stirring or shaking. Filter.		
	<b>Residue.</b> White crystal-line $\text{Mg}(\text{NH}_4)\text{AsO}_4 \cdot 6\text{H}_2\text{O}$ . <b>As</b> <b>present.</b>	<b>Filtrate.</b> May contain Au, Mo, Se and Te as chlorides or acids. Concentrate to remove ammonia, boil with several ml. of saturated oxalic acid solution, dilute, boil and filter. Extract ppt. with HCl to remove coprecipitated tellurous acid.	
	<b>Residue.</b> Brownish-black or purplish-black. <b>Au</b> <b>present.</b>	<b>Filtrate.</b> Concentrate with strong HCl on a water bath and, after removing the precipitated KCl, treat with a slight excess of solid $\text{Na}_2\text{SO}_3$ . Filter.	
		<b>Residue.</b> Red. <b>Se</b> <b>present.</b>	<b>Filtrate.</b> Dilute with an equal volume of water, and add successively a little KI solution and excess of solid $\text{Na}_2\text{SO}_3$ , whereby the $\text{K}_2[\text{TeI}_6]$ is reduced to Te. Filter.
		<b>Residue.</b> Black. <b>Te</b> <b>present.</b>	<b>Filtrate.</b> Boil with HCl to remove dissolved $\text{SO}_2$ and treat successively with 10 per cent $\text{NH}_4\text{SCN}$ solution and a little $\text{SnCl}_2$ solution. Red coloration, soluble in ether. <b>Mo present.</b> Confirm by potassium xanthate test or by the $\alpha$ -benzoin oxime test.

If Pt, Au, Se and Te are known to be absent, Table IV may be simplified as follows.

Boil the Group ppt. with 5 ml. of concentrated HCl for 5 minutes, dilute with 2-3 ml. of water, pass $H_2S$ for 1 minute (to reprecipitate small amounts of As that may have dissolved) and filter.		
<b>Residue.</b> May contain $As_2S_3$ (or $As_2S_5$ ) and $MoS_3$ . Wash with dilute HCl, followed by water; reject the washings. Warm the ppt. with 3-4 ml. of 4N $NH_3$ solution for 3 minutes, and filter.		<b>Filtrate.</b> May contain Sb and Sn as chlorides or complex chloro-acids. Examine by Table VI (Section VII, 11).
<b>Residue.</b> May contain undissolved $MoS_3$ . Dissolve in concentrated HCl and $Br_2$ water, and boil to expel $Br_2$ . Test for Mo by the $NH_4SCN-SnCl_2$ reaction.	<b>Filtrate.</b> May contain As and some of the Mo. Identify As as in Table VI (Section VII, 11) or by the Gutzeit test (Section III, 13). Identify Mo thus: acidify a portion of the filtrate with dilute HCl and add a little solid potassium xanthate. A red-purple coloration confirms Mo.	

*Note.* If the alternative potassium hydroxide method is employed for the separation of Groups IIA and IIB, the KOH extract may contain As, Sb, Sn, Se, Te and part of the Mo; the residue may contain, in addition to  $HgS$ ,  $PbS$ ,  $Bi_2S_3$ ,  $CuS$ ,  $CdS$  and  $PdS$ , the gold and platinum partly as sulphides and possibly partly in the form of the free metals. Mo is readily identified by the potassium xanthate or  $\alpha$ -benzoin oxime test. The Au and Pt will accompany  $HgS$  after extraction with dilute nitric acid: upon dissolution in aqua regia, Pt may be identified and removed as  $K_2[PtCl_6]$  and the Au with oxalic acid. Pd is identified as the dimethylglyoxime complex in the presence of  $N$  hydrochloric acid after the Pb, Bi, Cu and Cd have been removed.

#### VANADIUM, V

The most important compounds of vanadium are derived from the oxides  $V_2O_4$  and  $V_2O_5$ , both of which exhibit acidic properties, but the latter to the greater degree. Vanadium pentoxide, the anhydride of vanadic acid, is only slightly soluble in water, but dissolves readily in concentrated solutions of caustic alkalis, forming vanadates. Vanadic acid, like phosphoric acid, exists in the form of meta-, pyro- and ortho-compounds ( $HVO_3$ ,  $H_4V_2O_7$ , and  $H_5VO_4$  respectively). Unlike the salts of phosphoric acid, the meta-vanadates are the most stable and the ortho-vanadates the least stable. A solution of an ortho-vanadate passes on boiling into the meta-vanadate, the pyro-salt being formed intermediately.

#### IX, 11.

#### REACTIONS OF VANADATES

Use a solution of ammonium (meta-) vanadate,  $NH_4VO_3$ , or the more soluble sodium meta-vanadate,  $NaVO_3$ .

1. **Hydrogen Sulphide.**—No precipitate is produced in acid solution, but a blue solution (due to the production of a quadrivalent

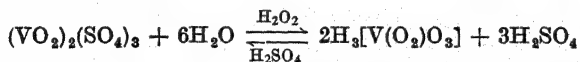
vanadium compound) is formed and sulphur separates. Other reducing agents, such as sulphur dioxide, oxalic acid, ferrous sulphate, hydrazine, formic acid and ethyl alcohol, also yield the blue vanadium (IV) salts (compare Molybdates, Section IX, 4). The reaction takes place slowly in the cold, but more rapidly on warming.

**2. Zinc, Cadmium or Aluminium in Acid Solution.**—These carry the reduction still further. The solutions turn at first blue (vanadyl salt—quadrivalent vanadium), then green (tervalent vanadium) and finally violet (bivalent vanadium).

**3. Ammonium Sulphide Solution.**—The solution is coloured claret-red, due to the formation of thiovanadates {probably  $(\text{NH}_4)_3\text{VS}_4$ }. Upon acidification of the solution, brown vanadium sulphide  $\text{V}_2\text{S}_5$  is incompletely precipitated, and the filtrate usually has a blue colour. The precipitate is soluble in solutions of alkalis, alkali carbonates and sulphides.

**4. Hydrogen Peroxide.**—A red coloration is produced when a few drops of hydrogen peroxide solution are added dropwise to an acid (15–20 per cent sulphuric acid) solution of a vanadate; excess of hydrogen peroxide should be avoided. The colour is not removed by shaking the solution with ether nor is it affected by phosphates or fluorides (distinction from titanium).

The red colour is probably due to the per-salt  $(\text{VO}_2)_2(\text{SO}_4)_3$ , which is converted by excess of hydrogen peroxide into the yellow ortho peroxy-vanadic acid  $\text{H}_3[\text{V}(\text{O}_2)\text{O}_3]$ , hence excess of hydrogen peroxide must be avoided.



† The spot-test technique is as follows. Mix a drop of 15–20 per cent sulphuric acid and a drop of the test solution either on a spot plate or in a porcelain micro crucible. After a few minutes add 1 drop of 1 per cent hydrogen peroxide solution and then another drop, if necessary. A red to pink coloration appears.

Sensitivity: 2.5  $\mu\text{g}$ . V. Concentration limit: 1 in 20,000.

Molybdates, chromates, iodides, bromides, ceric salts and also large amounts of coloured metallic salts reduce the sensitivity of the reaction.

**5. Ammonium Chloride.**—The addition of solid ammonium chloride to a solution of an alkali vanadate results in the separation of colourless, crystalline ammonium vanadate  $\text{NH}_4\text{VO}_3$ , sparingly soluble in a concentrated solution of ammonium chloride.

**6. Lead Acetate Solution:** yellow precipitate of lead vanadate, turning white or pale yellow on standing; the precipitate is insoluble in dilute acetic acid but soluble in dilute nitric acid.

**7. Barium Chloride Solution:** yellow precipitate of barium vanadate (distinction from arsenate and phosphate), soluble in dilute hydrochloric acid.

8. **Copper Sulphate Solution:** green precipitate with meta-vanadates. Pyro-vanadates give a yellow precipitate.

9. **Mercurous Nitrate Solution:** white precipitate of mercurous vanadate from neutral solutions.

10. **Ammonia Solution.**—When this reagent is added to a solution of a salt containing quadrivalent vanadium (*e.g.* that produced by reduction of a vanadate with hydrogen sulphide), dark grey hypovanadic acid  $\text{H}_2\text{VO}_3$  is formed; the precipitation is not complete unless excess of ferric chloride be present.

11. **Ammonium Molybdate Solution.**—No precipitate is produced in the presence of ammonium nitrate and nitric acid, a soluble molybdo-vanadate being formed (compare phosphate). If the vanadate is mixed with a phosphate, much of the vanadium is co-precipitated with the ammonium phospho-molybdate.

12. **Potassium Chlorate-*p*-Phenetidine Test.**—Vanadium catalyses the reaction between *p*-phenetidine ( $\text{H}_2\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OC}_2\text{H}_5$ , 1 : 4) and potassium chlorate: potassium hydrogen tartrate has an activating effect upon the reaction.

Treat 0.5 ml. of the test solution in a semimicro test-tube with 0.05 gram of potassium hydrogen tartrate, 1 ml. of the *p*-phenetidine reagent, 1 ml. of saturated potassium chlorate solution and dilute to 5 ml. with distilled water. Immerse the test-tube in a water bath: a violet colour appears within a few minutes.

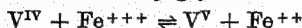
Lead interferes but is rendered harmless with 100 mg. of  $\text{Na}_2\text{SO}_4$ ; ferric iron also interferes and is rendered innocuous by adding 50 mg. of  $\text{NaNO}_3$ . A similar result is obtained by replacing  $\text{KClO}_3$  with a saturated solution of  $\text{KBrO}_3$ , but iodide as well as lead and ferric iron interfere.

Sensitivity: 0.001  $\mu\text{g. V}$ .

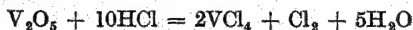
The *p*-phenetidine reagent consists of a 0.1 per cent solution of *p*-phenetidine in *N* hydrochloric acid.

13. **Tannin Test.**—When a neutral or acetic acid solution of a vanadate is treated with an excess of 10 per cent tannin solution, a deep blue (or blue-black) coloration is obtained. If ammonium acetate is present, a dark blue (or blue-black) precipitate separates. The precipitate or coloration is destroyed by mineral acids.

†14. **Ferric Chloride-Dimethylglyoxime Test.**—The reaction:



proceeds from left to right in alkaline solution and in the reverse direction in acid solution. The test for vanadates utilises the deep red coloration with dimethylglyoxime given by ferrous salts (compare Ferrous Iron, Section III, 19, reaction 10) and the fact that vanadates are readily reduced to the quadrivalent state by heating with concentrated hydrochloric acid:



All oxidising agents interfere and must be removed.

Evaporate 1 drop of the test solution and 2 drops of concentrated hydrochloric acid in a micro crucible *almost* to dryness. When cold, add a drop of 1 per cent ferric chloride solution, followed by 3 drops of a 1 per cent alcoholic solution of dimethylglyoxime, and render the mixture alkaline with ammonia solution. Dip a strip of quantitative filter paper or of drop-reaction paper into the solution. The precipitated ferric hydroxide remains behind and the red solution of ferrous dimethylglyoxime diffuses up the capillaries of the paper.

Sensitivity: 1  $\mu$ g. V. Concentration limit: 1 in 50,000.

### Dry Test

*Borax bead*: oxidising flame—colourless (yellow in the presence of much vanadium); reducing flame—green.

**Separation.**—Vanadates are not precipitated by  $\text{H}_2\text{S}$  in acid solution; reduction to the quadrivalent state occurs. With ammonium sulphide solution, the soluble thio-salt is formed, from which brown  $\text{V}_2\text{S}_5$  is precipitated by pouring into 6*N*  $\text{H}_2\text{SO}_4$ . The precipitate may be dissolved in concentrated  $\text{HCl}$ , and reactions 4 and 12 applied.

In general, however, the vanadyl salt present in the filtrate from Group II will be largely re-oxidised to vanadate by the nitric acid treatment before the precipitation of Group IIIA. If the solution contains the cations of Group IIIA and certain members of later groups, the vanadates of these metals may be precipitated. However, if no other member of Group IIIA is present, vanadium may be incompletely precipitated as ammonium vanadate. It is therefore recommended where vanadium is suspected (pale-blue solution left after the passage of hydrogen sulphide in Group II) that the Group II filtrate be tested for iron with potassium ferrocyanide solution. If iron is absent, some ferric chloride solution should be added before precipitation of Group IIIA.

See also Table V in Section IX, 18.

### BERYLLIUM (OR GLUCINUM), Be

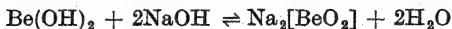
Beryllium is a divalent metal and closely resembles aluminium in chemical properties; it also exhibits resemblances to the alkaline earth metals. The salts react acid in aqueous solution, and possess a sweet taste (hence the name glucinum formerly given to the element). Beryllium compounds are **highly poisonous**.

## IX, 12. REACTIONS OF BERYLLIUM COMPOUNDS

Use a solution of beryllium sulphate,  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ .

**1. Ammonia or Ammonium Sulphide Solution:** white precipitate of beryllium hydroxide  $\text{Be}(\text{OH})_2$ , similar in appearance to aluminium hydroxide, insoluble in excess of the reagent, but readily soluble in dilute hydrochloric acid, forming a colourless solution. Precipitation is prevented by tartrates and citrates.

**2. Sodium Hydroxide Solution:** white gelatinous precipitate of beryllium hydroxide, readily soluble in excess of the precipitant, forming sodium beryllate  $\text{Na}_2[\text{BeO}_2]$ ; on boiling the latter solution (best when largely diluted), beryllium hydroxide is reprecipitated (distinction from aluminium). The precipitate is also soluble in 10 per cent sodium bicarbonate solution (distinction from aluminium).



On the other hand, the precipitate is insoluble in aqueous ethylamine solution whereas aluminium hydroxide dissolves in a moderate excess of the reagent. Precipitation is prevented by tartrates and citrates.

**3. Ammonium Carbonate Solution:** white precipitate of basic beryllium carbonate, soluble in excess of the reagent (difference from aluminium). On boiling the solution, the white basic carbonate is re-precipitated.

**4. Oxalic Acid or Ammonium Oxalate Solution:** no precipitate (difference from thorium, zirconium and cerium).

**5. Sodium Thiosulphate Solution:** no precipitate (difference from aluminium).

**6. Basic Acetate-Chloroform Test.**—Upon dissolving beryllium hydroxide (reaction 1) in glacial acetic acid and evaporating to dryness with a little water, basic beryllium acetate  $\text{BeO} \cdot 3\text{Be}(\text{C}_2\text{H}_3\text{O}_2)_2$  is produced, which dissolves readily upon extraction with chloroform. This forms the basis of a method for separating beryllium from aluminium, since basic aluminium acetate is insoluble in chloroform. The mixed hydroxides are treated as detailed above.

**†7. Quinalizarin Reagent\*:** cornflower-blue coloration with faintly alkaline solutions of beryllium salts. The reagent alone gives a characteristic violet colour with dilute alkali; but this is quite distinct from the blue of the beryllium complex: a blank test will render the difference clearly apparent.

Antimony, zinc and aluminium salts do not interfere; aluminium should, however, be kept in solution by the addition of sufficient sodium hydroxide; the influence of copper, nickel and cobalt salts can be eliminated by the addition of potassium cyanide solution; iron salts are "masked" by the addition of a tartrate but if aluminium salts are also present a red colour is produced. Magnesium salts give a similar blue colour, but beryllium can be detected in the presence of this element by utilising the fact that in ammoniacal solution the magnesium colour alone is completely destroyed by bromine water.

In adjacent depressions of a spot plate place a drop of the test solution and a drop of distilled water, and add a drop of the freshly prepared quinalizarin reagent to each. A blue coloration or precipitate, quite distinct from the violet colour of the reagent, is obtained.

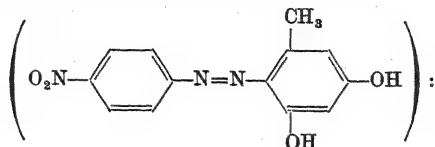
Sensitivity: 0.15  $\mu\text{g}$ . Be. Concentration limit: 1 in 350,000.

\* See under Aluminium, Section III, 21, reaction 10.

If **magnesium is present**, treat a drop of the solution on a spot plate with 2 drops of the reagent and 1 ml. of saturated bromine water. The original deep blue colour becomes paler when the bromine is added, but remains more or less permanently blue.

The reagent is prepared by dissolving 0.05 grams of quinalizarin in 100 ml. of 0.1*N* sodium hydroxide.

†3. **para-Nitrobenzene-azo-orcinol Reagent**



orange-red lake with beryllium salts in alkaline solution. Magnesium salts yield a brownish-yellow precipitate; salts and hydroxides of the rare earths, aluminium and alkaline earths are without influence; the interfering effect of silver, copper, cadmium, nickel, cobalt and zinc is eliminated by the addition of potassium cyanide solution.

Place a drop of the reagent on drop-reaction paper and into the middle of the resulting yellow area introduce the tip of a capillary containing the test solution so that the latter runs slowly on to the paper. Treat the stain with a further drop of the reagent. The stain is coloured deep orange-red.

Sensitivity: 0.2  $\mu\text{g}$ . Be. Concentration limit: 1 in 200,000.

The reagent consists of a 0.025 per cent solution of *p*-nitrobenzene-azo-orcinol in *N* sodium hydroxide.

†9. **Acetylacetone Test.**—Acetylacetone reacts with beryllium salts to yield the complex  $\text{Be}(\text{C}_5\text{H}_7\text{O}_2)_2$ , which possesses a highly characteristic appearance under the microscope.



Place a drop of the test solution on a microscope slide and add a drop of acetylacetone. Crystals separate immediately: these will be found to possess rhombic and hexagonal forms when observed under the microscope (magnification: *ca.* 75 diameters).

Concentration limit: 1 in 10,000.

## Dry Test

Upon heating beryllium salts with a few drops of cobalt nitrate solution upon charcoal, a grey mass is obtained (difference from aluminium).

**Separation.**—Beryllium is precipitated in Group IIIA. It is ultimately associated with aluminium in solution as sodium aluminate and sodium beryllate respectively. Upon diluting and boiling, only the  $\text{Be}(\text{OH})_2$  is precipitated. Alternatively, the quinalizarin test 7 may be applied to the solution or the basic acetate-chloroform test 6 to the mixed hydroxides. Beryllium may

also be detected in the presence of aluminium by the acetylacetone test 9; this is specific for Be.

Aluminium and beryllium are separated most satisfactorily by means of 8-hydroxyquinoline ("oxine") reagent; aluminium "oxinate" is precipitated in the presence of an ammonium acetate-acetic acid buffer solution, whereas beryllium "oxinate" is soluble in acetic acid. For this purpose, the alcoholic solution of the reagent (compare Magnesium, Section III, 33, reaction 7) should not be employed as the aluminium complex is slightly soluble in alcohol. The solution of sodium aluminate and beryllate is just acidified with dilute hydrochloric acid, a slight excess of the "oxine" solution added, followed by 5 ml. of saturated ammonium acetate solution. The precipitate of the aluminium complex  $\text{Al}(\text{C}_9\text{H}_6\text{ON})_3$  is filtered off. The filtrate is heated nearly to boiling and a slight excess of ammonia solution added. The production of a precipitate (beryllia), usually coloured brown or yellow by adsorbed "oxine," indicates the presence of beryllium.

The *precipitating reagent* consists of a 2 per cent solution of "oxine" in 2N acetic acid to which ammonia solution is added until a permanent precipitate is produced, and the latter is redissolved by warming.

Another method for separating beryllium and aluminium consists in adding excess of a solution of sodium fluoride to the solution. The complex sodium aluminofluoride  $\text{Na}_3[\text{AlF}_6]$  is formed in which the aluminium is present as a complex ion and from which the metal is not precipitated as hydroxide by ammonia solution. Beryllium is, however, readily precipitated as the hydroxide under these conditions.

See also Note 6 to Table V in Section IX, 18.

#### TITANIUM, Ti

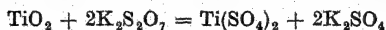
The most important compounds of titanium are those corresponding to the two oxides  $\text{Ti}_2\text{O}_3$  and  $\text{TiO}_2$ , and are termed titanous and titanic compounds respectively. The former usually yield violet aqueous solutions, and are powerful reducing agents; they behave like iron and aluminium compounds towards the common reagents. The latter are usually colourless, and are more frequently encountered in analytical work.

### IX, 13. REACTIONS OF TITANIC COMPOUNDS

Use a solution of titanic sulphate,  $\text{Ti}(\text{SO}_4)_2$ .\*

**1. Solutions of Sodium Hydroxide, Ammonia or Ammonium Sulphide.**—All these reagents give a white gelatinous precipitate of ortho-titanic acid  $\text{H}_4\text{TiO}_4$  or  $\text{Ti}(\text{OH})_4$  in the cold,

\* This may be prepared by fusing the dioxide  $\text{TiO}_2$  with a 12–15 fold excess of potassium pyrosulphate  $\text{K}_2\text{S}_2\text{O}_7$ . The melt, after powdering, is extracted with cold dilute  $\text{H}_2\text{SO}_4$  (say, 5 per cent) and filtered, if necessary.





almost insoluble in excess of the reagent, but soluble in mineral acids. If precipitation takes place from hot solution, meta-titanic acid  $\text{H}_2\text{TiO}_3$  or  $\text{TiO} \cdot (\text{OH})_2$  is said to be formed, which is difficultly soluble in dilute acids. Tartrates and citrates inhibit precipitation.

2. **Water.**—A white precipitate of meta-titanic acid is obtained on boiling a solution of a titanic salt with excess of water.

3. **Sodium Phosphate Solution:** white precipitate of titanium phosphate  $\text{Ti}(\text{HPO}_4)_2$  in dilute sulphuric acid solution.

4. **Zinc, Cadmium or Tin.**—When any of these metals is added to an acid (preferably hydrochloric acid) solution of a titanic salt, a violet coloration is produced, due to reduction to the titanous state. No reduction occurs with sulphur dioxide or with hydrogen sulphide.

5. **Cupferron Reagent\*:** flocculent yellow precipitate of the titanium salt,  $\text{Ti}(\text{C}_6\text{H}_5\text{O}_2\text{N}_2)_4$ , in acid solution (distinction from aluminium and beryllium). If *iron is present*, it can be removed by precipitation with ammonia and ammonium sulphide solutions in the presence of a tartrate; the titanium may then be precipitated from the acidified solution by cupferron.

6. **Hydrogen Peroxide.**—An orange-red coloration is produced in slightly acid solution. The colour is yellow with very dilute solutions. The coloration has been variously attributed to per-titanic acid  $\text{TiO}_3 \cdot n\text{H}_2\text{O}$  or to peroxo-disulphato-titanic acid  $\text{H}_2[\text{TiO}_2(\text{SO}_4)_2]$ .

Chromates, vanadates and cerium salts give colour reactions with the reagent and should therefore be absent. Iron salts give a yellow colour with hydrogen peroxide, but this is eliminated by the addition of syrupy phosphoric acid. Fluorides bleach the colour (stable  $[\text{TiF}_6]^-$  ions are formed), and large amounts of nitrates, chlorides, bromides and acetates as well as coloured ions reduce the sensitivity of the test. A decrease in the intensity of the yellow coloration upon the addition of ammonium fluoride indicates the presence of titanium.

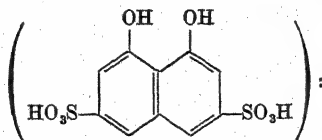
† The spot-test technique is as follows. Place a drop of the sulphuric acid test solution on a spot plate and add a drop of "10-volume" hydrogen peroxide. A yellow coloration results.

Sensitivity: 2  $\mu\text{g}$ . Ti. Concentration limit: 1 in 25,000.

The test is conducted on the semimicro scale as follows. Place 0.5 ml. of the test solution in a small test-tube, add 2 drops of dilute sulphuric acid and 1 drop of 3 per cent hydrogen peroxide solution. An orange-yellow or orange-red coloration is produced. Introduce a small crystal of ammonium fluoride; the colour disappears.

\* For the preparation of the reagent, see under Iron, Section III, 20, reaction 9.

## †7. Chromotropic Acid\* Reagent



reddish-brown coloration with titanium salts in the presence of hydrochloric or sulphuric acid. Appreciable concentrations of nitric acid inhibit the reaction.

Mix a drop of the test solution and a drop of the reagent on drop-reaction paper or upon a spot plate. A reddish-brown (or purplish-pink) spot or coloration results.

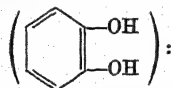
Sensitivity: 5  $\mu\text{g. TiO}_2$ . Concentration limit: 1 in 10,000.

Uranyl and ferric salts interfere and yield brown and deep green colorations respectively; these colours are destroyed by the addition of stannous chloride, for uranous and ferrous salts do not react with chromotropic acid. Mercury salts give a yellow and silver salts a black stain on drop-reaction paper; the colour due to titanium is, however, still perceptible.

In the presence of uranyl salts and/or ferric salts, proceed as follows. Mix a large drop of the test solution on a watch glass with a small quantity of a solution of stannous chloride in hydrochloric acid (a large excess is to be avoided) and warm gently (hot plate). Place a drop of the reagent on some drop-reaction paper and then a drop of the clear solution from the watch glass. A reddish-brown (or purplish-pink) spot appears.

The reagent consists of a 5 per cent aqueous solution of chromotropic acid. The reagent does not keep well, hence it is preferable to impregnate drop-reaction paper with the reagent solution and allow the paper to dry in the air. The impregnated papers are stable for several months. In use, a drop of the test solution and a drop of  $N \text{ H}_2\text{SO}_4$  are placed upon the impregnated paper: a purplish-pink colour results.

## †8. Pyrocatechol Reagent



yellow coloration with neutral or weakly acid (sulphuric acid) solutions of titanium salts. Ferric, chromium, cobalt and nickel salts interfere as do also large amounts of free mineral acids: alkali hydroxides and carbonates reduce the sensitivity of the test.

Place a drop of the sulphuric acid test solution on drop-reaction paper impregnated with the reagent. A yellow or yellowish-red spot is obtained.

Sensitivity: 3  $\mu\text{g. Ti}$ . Concentration limit: 1 in 20,000.

The reagent consists of a freshly prepared 10 per cent aqueous solution of pyrocatechol.

\* Or 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid.

**Dry Test**

*Microcosmic salt bead*: oxidising flame—colourless; reducing flame—yellow whilst hot and violet when cold (this result is obtained more rapidly if a little stannous chloride is added). If the bead is heated in the reducing flame with a trace of ferrous sulphate, it acquires a blood-red colour.

**Separation.**—If sufficient acid is present in the earlier groups to prevent its separation by hydrolysis, titanium is found in Group IIIA. It can be readily detected in the precipitate obtained after treatment with  $\text{Na}_2\text{O}_2$  by means of the hydrogen peroxide test 6;  $\text{NH}_4\text{F}$  solution will discharge the colour. It is usually best to fuse the precipitate with 10 times its weight of powdered  $\text{K}_2\text{S}_2\text{O}_7$  or  $\text{KHSO}_4$ ; the melt, containing the metals as sulphates, is extracted with cold water, and the extract boiled for about 30 minutes. Meta-titanic acid separates out. This is filtered off, dissolved in concentrated  $\text{HCl}$  and the  $\text{H}_2\text{O}_2$  test applied.

See also Table V in Section IX, 18.

**ZIRCONIUM, Zr**

Zirconium\* forms only one important oxide, zirconia  $\text{ZrO}_2$ , which is amphoteric in character. The normal zirconium salts, like  $\text{ZrCl}_4$ , are readily hydrolysed in solution giving rise chiefly to zirconyl salts, containing the bivalent radical  $\text{ZrO}^{\text{II}}$ . The zirconates, e.g.  $\text{Na}_2\text{ZrO}_3$ , are best produced from  $\text{ZrO}_2$  by fusion methods. Zirconium also readily forms complex salts, e.g. potassium fluozirconate  $\text{K}_2[\text{ZrF}_6]$ , produced by fusing zirconia with potassium hydrogen fluoride.

Ignited zirconium dioxide, or the mineral, is insoluble in all acids except hydrofluoric acid. It is soluble in fused caustic alkalis and in sodium carbonate; the resulting alkali zirconate is practically insoluble in water, being converted into zirconium hydroxide by this solvent. It is therefore best dissolved in hydrochloric acid, and the zirconium hydroxides precipitated by ammonia solution, etc.

**IX, 14. REACTIONS OF ZIRCONIUM COMPOUNDS**

Use a solution of zirconyl nitrate  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  or of zirconyl chloride  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ .

**1. Sodium Hydroxide Solution**: white, gelatinous precipitate of the hydroxide  $\text{Zr}(\text{OH})_4$  (or  $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$ ) in the cold, practically insoluble in excess of the reagent (difference from aluminium and beryllium), but soluble in dilute mineral acids (avoid sulphuric acid). With a hot solution of a zirconium salt, a white precipitate of  $\text{ZrO}(\text{OH})_2$  is obtained; it is sparingly soluble in dilute but soluble in concentrated mineral acids. Tartrates and citrates inhibit the precipitation of the hydroxide.

**2. Ammonia or Ammonium Sulphide Solution**: white, gelatinous precipitate of the hydroxide  $\text{Zr}(\text{OH})_4$  (or  $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$ ), insoluble in excess of the reagent.

\* Small quantities of hafnium are always present; the two elements cannot, at present, be differentiated by qualitative analysis (see, however, Section X, 4).

**3. Sodium Phosphate Solution:** white precipitate of zirconium phosphate,  $\text{Zr}(\text{HPO}_4)_2$  or  $\text{ZrO}(\text{H}_2\text{PO}_4)_2$ , even in solutions containing 10 per cent of sulphuric acid by weight and also tartrates and citrates. No other element forms an insoluble phosphate under these conditions except titanium. The latter element can be kept in solution as the so-called "per-titanic acid" by the addition of sufficient hydrogen peroxide solution, preferably of "100-volume" strength, before the sodium phosphate is introduced.

**4. Hydrogen Peroxide:** white precipitate of zirconium "peroxide" from slightly acid solutions; this liberates chlorine when warmed with concentrated hydrochloric acid. When both hydrogen peroxide and sodium phosphate are added to a solution containing zirconium, the precipitate is zirconium phosphate (see reaction 3).

**5. Ammonium Carbonate Solution:** white precipitate of basic zirconium carbonate, readily soluble in excess of the reagent, but reprecipitated on boiling.

**6. Oxalic Acid Solution:** white precipitate of zirconium oxalate, readily soluble in excess of the reagent and also in ammonium oxalate solution (difference from thorium).

**7. Ammonium Oxalate Solution:** white precipitate of zirconium oxalate, soluble in excess of the reagent (distinction from aluminium and beryllium); the solution gives no precipitate with hydrochloric acid (difference from thorium).

*Note.* A solution of zirconium sulphate or a zirconium salt solution containing excess of sulphate ions does not give a precipitate with either ammonium oxalate or oxalic acid. This is due to the fact that the zirconium is present as the anion  $[\text{ZrO}(\text{SO}_4)_2]^-$ , hence sulphuric acid should be avoided in preparing solutions of zirconium salts.

**8. Saturated Potassium Sulphate Solution:** white precipitate of  $\text{K}_2[\text{ZrO}(\text{SO}_4)_2]$ , insoluble in excess of the reagent. When precipitation takes place in boiling solution, the resulting basic zirconium sulphate is insoluble in dilute hydrochloric acid (difference from thorium and cerium). No precipitate is obtained with sodium sulphate solution.

**9. Phenylarsonic Acid Reagent**  $\{\text{C}_6\text{H}_5\cdot\text{AsO}(\text{OH})_2\}$ : white precipitate of zirconium phenylarsonate in the presence of 0.5–1*N* hydrochloric acid; it is best to boil the solution. Tin and thorium salts must be absent.

The reagent consists of a 10 per cent aqueous solution of phenylarsonic acid.

#### 10. normal-Propylarsonic Acid Reagent



white precipitate of zirconium *n*-propylarsonate in dilute sulphuric acid solution (separation from most other metals including titanium but not tin).

The reagent consists of a 5 per cent aqueous solution of *n*-propylarsonic acid.

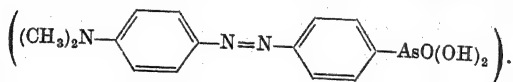
**11. Potassium or Sodium Iodate Solution.**—In faintly acid solution, a voluminous, white precipitate of basic zirconium iodate is obtained. The precipitate is soluble in warm hydrochloric acid (difference from aluminium).

†12. **Alizarin-S\* Reagent:** red precipitate in a strongly acid medium. Fluorides discharge the colour because of the formation of the stable zirconium-fluoride anion  $[\text{ZrF}_6]^{--}$ .

Place a drop of the test solution (which has been acidified with hydrochloric acid) on a spot plate, add a drop of the reagent and a drop of concentrated hydrochloric acid. A red precipitate results.

The reagent consists of a 1 per cent aqueous solution of alizarin-S (sodium alizarin sulphonate).

†13. **para - Dimethylaminobenzene - azo - phenylarsonic Acid Reagent**



Acid solutions of zirconium salts give a brown precipitate with the reagent. If the test be conducted on filter paper, the brown precipitate remains in the pores of the paper and the excess of the coloured reagent may be washed out with dilute acid.

Impregnate some drop-reaction paper with the reagent and dry the paper. Place a drop of the acid test solution on the paper. Dip the paper into 2N hydrochloric acid at 50–60°C. A brown spot or ring remains.

Sensitivity: 0.1  $\mu\text{g}$ . Zr (in N HCl). Concentration limit: 1 in 500,000.

Free sulphuric acid exceeding *N* in concentration reduces the sensitivity of the test; phosphates, fluorides and organic acids, which form precipitates or stable complex compounds, either inhibit or retard the reaction; molybdates, tungstates and salts of titanium or cerium give precipitates, but their interference can be eliminated by mixing the test solution with about an equal volume of concentrated hydrochloric acid, adding some "100-volume" hydrogen peroxide, spotting the mixture on to impregnated drop-reaction paper and finally washing the latter with warm 2N hydrochloric acid. Tin also gives a coloured precipitate, but this may be prevented by the above treatment and omitting the hydrogen peroxide; a brown ring, surrounding a central zone, is obtained.

The reagent is prepared by dissolving 0.1 gram of *p*-dimethylamino-benzene-azo-phenylarsonic acid in 5 ml. of concentrated hydrochloric acid and 100 ml. of ethyl alcohol.

### Dry Tests

No characteristic results are obtained with the borax or microcosmic beads nor does zirconium yield a distinguishing flame test.

\* For formula, see under Aluminium, Section III, 21, reaction 9.

**Separation.**—Zirconium is precipitated in Group IIIA as  $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$ , if phosphates are absent. It can be readily detected in the residue obtained after treating the Group IIIA precipitate with 10 per cent sodium hydroxide solution and "20- or 40-volume" hydrogen peroxide. The residue is dissolved in hydrochloric acid and boiled to expel chlorine. The resulting solution is treated with sodium phosphate solution and hydrogen peroxide, when a white precipitate indicates the presence of *zirconium* and an orange-yellow coloration the presence of *titanium* (see reaction 3 above). Alternatively, the alizarin-S test (reaction 12) may be applied to the solution in hydrochloric acid.

See also Table V, Section IX, 18.

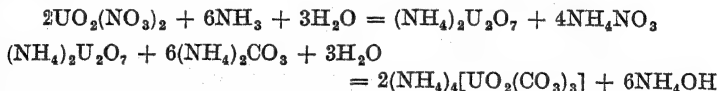
#### URANIUM, U

The most important uranium compounds are the uranyl salts, which contain the bivalent radical uranyl  $\text{UO}_2^{2+}$ , and the uranates  $\text{M}_2\text{U}_2\text{O}_7$ , analogous to the pyrosulphates  $\text{M}_2\text{S}_2\text{O}_7$  and the dichromates  $\text{M}_2\text{Cr}_2\text{O}_7$ . Only the reactions of the former will be described.

### IX, 15. REACTIONS OF URANYL COMPOUNDS

Use a solution of uranyl nitrate,  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , or of uranyl acetate,  $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ .

**1. Ammonia Solution:** yellow precipitate of ammonium di-uranate  $(\text{NH}_4)_2\text{U}_2\text{O}_7$ , insoluble in excess of the reagent, but readily soluble in ammonium carbonate solution.



The sparingly soluble ammonium di-uranate is probably formed through the intermediate uranyl hydroxide  $\text{UO}_2(\text{OH})_2$ ; the latter passes by loss of water into di-uronic acid  $\{2\text{UO}_2(\text{OH})_2 = \text{H}_2\text{U}_2\text{O}_7 + \text{H}_2\text{O}\}$ , and thence into  $(\text{NH}_4)_2\text{U}_2\text{O}_7$ .

No precipitation occurs in the presence of certain organic acids, such as oxalic, tartaric and citric acids.

**2. Sodium Hydroxide Solution:** yellow amorphous precipitate of sodium di-uranate  $\text{Na}_2\text{U}_2\text{O}_7$ , soluble in ammonium carbonate solution.

**3. Ammonium Sulphide Solution:** brown precipitate of uranyl sulphide  $\text{UO}_2\text{S}$ , soluble in dilute acids and in ammonium carbonate solution.

**4. Hydrogen Peroxide:** pale-yellow precipitate of  $\text{UO}_4 \cdot x\text{H}_2\text{O}$ , soluble in ammonium carbonate solution with the formation of a deep yellow solution. Chromium, titanium and vanadium interfere with this otherwise sensitive test.

5. **Cupferron Reagent:** no precipitate (distinction from titanium).

6. **Sodium Phosphate Solution:** white precipitate of uranyl phosphate  $\text{UO}_2\text{HPO}_4$ , soluble in mineral acids but insoluble in dilute acetic acid. If precipitation is effected in the presence of ammonium sulphate or of ammonium acetate, uranyl ammonium phosphate  $\text{UO}_2(\text{NH}_4)\text{PO}_4$  is precipitated.

7. **Ammonium (or Sodium) Carbonate Solution:** white precipitate of uranyl carbonate  $\text{UO}_2\text{CO}_3$ , soluble in excess of the reagent forming a clear, yellow solution containing ammonium uranyl carbonate  $(\text{NH}_4)_4[\text{UO}_2(\text{CO}_3)_3]$ .

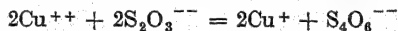
8. **Potassium Ferrocyanide Solution:** brown precipitate of uranyl ferrocyanide  $(\text{UO}_2)_2[\text{Fe}(\text{CN})_6]$  in neutral or acetic acid solutions, soluble in dilute hydrochloric acid (difference from copper). The precipitate becomes yellow upon the addition of sodium hydroxide solution, due to its conversion into sodium di-uranate (distinction from copper and from molybdenum ferrocyanide).



† The spot-test technique is as follows. Place a drop of the test solution on drop-reaction paper and add a drop of potassium ferrocyanide solution. A brown spot is obtained.

Sensitivity: 0.9  $\mu\text{g}$ . U. Concentration limit: 1 in 50,000.

Both iron and copper interfere. If, however, potassium iodide solution is added, they are reduced to the non-reactive ferrous and cuprous states; the liberated iodine may be decolourised with sodium thiosulphate solution. Alternatively, the reduction may be carried out with sodium thiosulphate solution alone on a spot plate, the copper acting as a catalyst for the reduction of the iron:



Place a drop of concentrated potassium iodide solution on a piece of drop-reaction paper and, after the iodide solution has soaked into the paper, add a drop of the acidified test solution. Add a further drop of the potassium iodide solution to complete the reduction, followed by a drop of sodium thiosulphate solution. Then add a drop of potassium ferrocyanide solution to the decolourised spot, whereupon a brown ring is obtained.

### Dry Test

*Borax or microcosmic salt bead:* oxidising flame—yellow; reducing flame—green.

**Separation.**—Uranium is precipitated in Group IIIA as  $(\text{NH}_4)_2\text{U}_2\text{O}_7$ . It is most simply separated from  $\text{Fe}(\text{OH})_3$ ,  $\text{Cr}(\text{OH})_3$  and  $\text{Al}(\text{OH})_3$  by digestion in the cold with a large excess of

ammonium carbonate solution. The ammonium di-uranate dissolves (see reaction 1 above); upon acidification with HCl and addition of  $K_4[Fe(CN)_6]$  solution, a brown precipitate is formed.

See also Table V in Section IX, 18.

#### THORIUM, Th

The analytically important compounds of thorium are derived from the dioxide  $ThO_2$ , i.e. contain quadrivalent thorium.

### IX, 16. REACTIONS OF THORIUM COMPOUNDS

Use a solution of thorium nitrate,  $Th(NO_3)_4 \cdot 4H_2O$ .

**1. Ammonia, Ammonium Sulphide or Sodium Hydroxide Solution:** white precipitate of thorium hydroxide  $Th(OH)_4$  or  $ThO_2 \cdot nH_2O$ , insoluble in excess of the reagent, but readily soluble in dilute acids when freshly precipitated. Tartrates and also citrates prevent the precipitation of the hydroxide.

**2. Ammonium or Sodium Carbonate Solution:** white precipitate of basic carbonate, readily soluble in excess of the concentrated reagent forming  $[Th(CO_3)_5]^{6-}$ .

**3. Oxalic Acid Solution:** white, crystalline precipitate of thorium oxalate  $Th(C_2O_4)_2 \cdot 6H_2O$  (distinction from aluminium and beryllium), insoluble in excess of the reagent and in 0.5N hydrochloric acid.

**4. Ammonium Oxalate Solution:** white precipitate of thorium oxalate, which dissolves on boiling with a large excess of the reagent forming  $[Th(C_2O_4)_3]^{2-}$ , but is reprecipitated upon the addition of hydrochloric acid (difference from zirconium).

**5. Saturated Potassium Sulphate Solution:** white precipitate of the complex salt  $K_4[Th(SO_4)_4] \cdot 2H_2O$ , insoluble in excess of the precipitant, but soluble in dilute hydrochloric acid.

**6. Hydrogen Peroxide:** white precipitate of hydrated thorium peroxide (variously formulated as  $ThO_3 \cdot 2H_2O$ ,  $Th(OH)_5O \cdot OH$  and  $Th_2O_7 \cdot 4H_2O$ ) in neutral or faintly acid solution.

**7. Sodium Thiosulphate Solution:** precipitate of thorium hydroxide and sulphur on boiling (distinction from cerium).

**8. Potassium Iodate Solution:** white, bulky precipitate of thorium iodate  $Th(IO_3)_4$ . Precipitation occurs in the presence of 50 per cent by volume of concentrated nitric acid (difference from cerous cerium).

**9. Potassium Ferrocyanide Solution:** white precipitate of thorium ferrocyanide  $Th[Fe(CN)_6]$  in neutral or slightly acid solution.



**10. Potassium Fluoride Solution:** bulky, white precipitate of thorium fluoride  $\text{ThF}_4$ , insoluble in excess of the reagent (distinction and method of separation from aluminium, beryllium, zirconium and titanium).

**11. Saturated Sebacic Acid Solution**  $\{\text{CO}_2\text{H} \cdot (\text{CH}_2)_8 \cdot \text{CO}_2\text{H}\}$ : white voluminous precipitate of thorium sebacate  $\text{Th}(\text{C}_{10}\text{H}_{18}\text{O}_4)_2$  (difference from cerium).

**12. meta-Nitrobenzoic Acid Reagent**  $(\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H})$ .—Upon addition of excess of the reagent to a neutral solution of a thorium salt at about  $80^\circ$ , a white precipitate of the salt  $\text{Th}(\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2)_4$  is obtained (distinction from cerium).

The reagent is prepared by dissolving 1 gram of the acid in 250 ml. of water at  $80^\circ$ , allowing to cool overnight and filtering.

There are no characteristic dry tests for thorium.

**Separation.**—See under Cerium (Section IX, 17B).

#### CERIUM, Ce

Cerium forms two well-defined series of salts, cerous and ceric, in which the element is trivalent and quadrivalent respectively. The cerium is more basic in the former than in the latter state, hence the cerous salts are the more stable.

### IX, 17A. REACTIONS OF CEROUS COMPOUNDS

Use a solution of cerous nitrate,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ .

**1. Ammonia or Ammonium Sulphide Solution:** *white* precipitate of cerous hydroxide  $\text{Ce}(\text{OH})_3$  (or  $\text{Ce}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ ), insoluble in excess of the precipitant, but readily soluble in acids. The precipitate slowly oxidises in the air, finally becoming converted into yellow ceric hydroxide  $\text{Ce}(\text{OH})_4$  (or  $\text{CeO}_2 \cdot n\text{H}_2\text{O}$ ). Sodium hydroxide solution gives a similar result. The precipitation is prevented by tartrates and citrates.

**2. Oxalic Acid or Ammonium Oxalate Solution:** white precipitate of cerous oxalate  $\text{Ce}_2(\text{C}_2\text{O}_4)_3$ , insoluble in excess of the reagent (compare thorium and zirconium), and in very dilute mineral acids.

**3. Sodium Thiosulphate Solution:** no precipitate (distinction from thorium and from ceric cerium).

**4. Saturated Potassium Sulphate Solution:** white, crystalline precipitate, having the composition  $\text{Ce}_2(\text{SO}_4)_3 \cdot 3\text{K}_2\text{SO}_4$  in neutral solution and  $\text{Ce}_2(\text{SO}_4)_3 \cdot 2\text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$  from slightly acid solution (difference from aluminium and beryllium).

**5. Sodium Bismuthate.**—This reagent, in the presence of dilute nitric acid, converts cerous into ceric salts in the cold. A similar

result is obtained by heating with ammonium persulphate or with lead dioxide and dilute nitric acid (1 : 2). In all cases, the solutions become yellow or orange in colour.

**6. Ammonium Carbonate Solution:** white precipitate of cerous carbonate  $\text{Ce}_2(\text{CO}_3)_3$ , nearly insoluble in excess of the precipitant (difference from beryllium, thorium and zirconium) and insoluble in sodium carbonate solution.

**7. Hydrogen Peroxide.**—When a cerous salt is treated with ammonia solution and excess of hydrogen peroxide is added a yellowish-brown or reddish-brown precipitate or coloration, due to cerium peroxide  $\text{Ce}(\text{OH})_3\text{O} \cdot \text{OH}$  or  $\text{CeO}_3 \cdot 2\text{H}_2\text{O}$ , is formed. This is not very stable. Upon boiling the mixture, yellow ceric hydroxide  $\text{Ce}(\text{OH})_4$  is obtained. The test cannot be applied directly in the presence of iron since the colour of ferric hydroxide is similar to that of ceric per-hydroxide. The precipitation of ferric hydroxide may be prevented by the addition of an alkali tartrate in consequence of the formation of complex ferri-tartrate ions; this, however, reduces the sensitivity of the test for cerium.

† The spot-test technique is as follows. Mix a drop of the hot test solution, of "10-volume" hydrogen peroxide and of dilute ammonia solution in a porcelain micro-crucible and warm gently. A yellow or yellowish-brown precipitate or coloration appears.

Sensitivity: 0.35  $\mu\text{g}$ . Ce. Concentration limit: 1 in 140,000.

**8. Ammonium Fluoride Solution:** white, gelatinous precipitate of cerous fluoride  $\text{CeF}_3$  in neutral or slightly acid solution. The precipitate becomes powdery upon standing.

**9. Potassium Iodate Solution:** white precipitate of cerous iodate  $\text{Ce}(\text{IO}_3)_3$  in neutral solution, soluble in nitric acid (difference from ceric iodate; compare thorium).

† **10. Ammoniacal Silver Nitrate Reagent.**—This reagent reacts with neutral solutions of cerous salts to form ceric hydroxide and metallic silver (difference from ceric cerium); the former is coloured black by the finely divided silver:



Ferric, manganous and cobaltous salts also give the higher metallic hydroxides and silver, and must therefore be absent.

Mix a drop of the neutral test solution and a drop of the reagent on a watch glass or in a porcelain micro crucible, and warm gently. A black precipitate or brown coloration appears.

Sensitivity: 1  $\mu\text{g}$ . Ce. Concentration limit: 1 in 50,000.

The ammoniacal silver nitrate reagent is prepared by treating ca. 0.4N silver nitrate with dilute ammonia solution until the precipitate first formed is just redissolved.

**IX, 17B. REACTIONS OF CERIC COMPOUNDS**

Use a solution of "ceric ammonium sulphate"



or of ceric sulphate  $\text{Ce}(\text{SO}_4)_2$  in dilute sulphuric acid.

**1. Ammonia or Sodium Hydroxide Solution:** *yellow* precipitate of ceric hydroxide  $\text{Ce}(\text{OH})_4$ . If the precipitate is warmed with hydrochloric acid, chlorine is evolved and cerous chloride is formed.

**2. Oxalic Acid or Ammonium Oxalate Solution:** reduction occurs, more rapidly on warming, to the cerous condition, and ultimately white cerous oxalate is precipitated.

**3. Saturated Potassium Sulphate Solution:** no precipitate (distinction from cerous salts).

**4. Reducing Agents** (*e.g.* hydrogen sulphide, sulphur dioxide, hydrogen peroxide and hydriodic acid).—These convert ceric salts into cerous salts.

**5. Sodium Thiosulphate Solution:** yellow colour of solution discharged and sulphur precipitated, owing to reduction.

**6. Ammonium Fluoride Solution:** yellow colour of solution is discharged but no precipitate is produced.

**7. Potassium Iodate Solution:** white precipitate of ceric iodate  $\text{Ce}(\text{IO}_3)_4$  from concentrated nitric acid solution (difference from cerous cerium; thorium and zirconium give a similar reaction).

**†8. Anthranilic Acid Reagent** ( $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , 1 : 2).—Ceric cerium oxidises anthranilic acid to a brown compound. Cerous cerium does not react and must be oxidised first with lead dioxide and concentrated nitric acid (8N) to the ceric state; other oxidising agents cannot be used since they react with the anthranilic acid. Ferric iron inhibits the test and must be masked by the addition of phosphoric acid. The ions of gold and vanadium, as well as chromate ion, react similarly and therefore interfere. Reducing agents must be absent.

Place a drop of the test solution (slightly acid with nitric acid) on a spot plate and add a drop of a 5 per cent solution of anthranilic acid in alcohol. A blackish-blue precipitate appears, which rapidly passes into a soluble product and colours the solution brown.

Concentration limit: 1 in 10,000.

**Dry Test**

**Borax Bead:** oxidising flame—dark brown whilst hot and light yellow to colourless when cold; reducing flame—colourless.

**Separation.**—Cerium and thorium salts are precipitated in Group IIIA. They may be separated from the other metals of the group by dissolving the precipitate in dilute HCl and adding oxalic acid solution, when the oxalates of both metals are precipitated. The thorium and cerium may be separated: (a) by dissolving the thorium oxalate in a mixture of ammonium acetate solution and acetic acid, cerium oxalate being insoluble under these conditions; (b) by treatment with a large excess of hot concentrated ammonium oxalate solution; only the thorium oxalate dissolves (a complex ion being formed), and may be reprecipitated from the resultant solution as oxalate by the addition of hydrochloric acid.

In routine qualitative analysis, it is probably best to boil the mixed oxalates (after washing with 2 per cent oxalic acid solution) with 5 per cent potassium hydroxide solution, thereby converting them into the hydroxides. The precipitate is separated by filtration, washed with hot water, dissolved in the minimum volume of dilute hydrochloric acid and the solution divided into two parts:

(i) **Th.**—Neutralise with ammonia solution, and add the meta-nitro-benzoic acid reagent (Section IX, 16, test 12) or a warm saturated solution of sebacic acid (*ibid.* test 11). Alternatively, add hydrochloric acid to the neutral solution until the concentration is about 0.3*N*, and then sodium pyrophosphate solution. A white precipitate,  $\text{ThP}_2\text{O}_7$ , indicates Th.

(ii) **Ce.**—Identify by the addition of hydrogen peroxide, followed by ammonia solution until the liquid is alkaline. A reddish-brown precipitate indicates Ce (see Section IX, 17A, reaction 7).

The following Table contains a scheme for the identification of the more common "rarer" elements (Ti, Zr, Ce, Th, V and U) in the presence of Fe, Al and Cr. If phosphate is present, it should be removed by the stannic chloride method (Section VIII, 2).

IX, 18. Table V.—Analysis of Group IIIA in the presence of Ti, Zr, Ce, Th, U and V

Dissolve the precipitate in the minimum volume of dilute HCl. Pour the weakly acid solution into an equal volume of a solution which contains 10 ml. of 6%  $\text{H}_2\text{O}_2$  and is 2.5N with respect to NaOH. (The latter solution should be freshly prepared.) Boil for 5 minutes, but no longer. Filter and wash the ppt. with hot 2%  $\text{NH}_4\text{NO}_3$  solution.

**Residue.** May contain  $\text{Fe}(\text{OH})_3$ ;  $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ ;  $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$ ;  $\text{ThO}_2 \cdot n\text{H}_2\text{O}$ ;  $\text{CeO}_2 \cdot n\text{H}_2\text{O}$  (and some  $\text{MnO}_2 \cdot n\text{H}_2\text{O}$ ).

Dissolve in dilute HCl, boil to expel  $\text{Cl}_2$  and divide the solution into five parts.

(i) Add KSCN solution (1).

Red coloration.

**Fe present.**

(ii) If Fe present, add just sufficient  $\text{H}_3\text{PO}_4$  (2) to decolorise the ferric salt, and then  $\text{H}_2\text{O}_2$ . Orange-red coloration, discharged by the addition of solid  $\text{NH}_4\text{F}$ .

**Ti present** (see Section IX, 13).

White ppt.

**Zr present** (3; see also Section IX, 14).

(iii) Add excess of saturated oxalic acid solution (ca. 10%). White ppt.

**Th and/or Ce present.**

For separation of Th and Ce, see Section IX, 17B.

(iv) Evaporate to fuming with  $\text{H}_2\text{SO}_4$  to expel HCl. Cool, dilute, add  $\text{HNO}_3$  and a little  $\text{NaBiO}_3$ . Stir and allow to stand.

Purple coloration.

**Mn present.**

**Filtrate.** May contain  $\text{Na}_2\text{CrO}_4$ ,  $\text{NaAlO}_2$ ,  $\text{Na}_3\text{VO}_4$  and sodium peruranate (probably  $\text{Na}_2\text{UO}_6$ ).

Acidify with dilute  $\text{HNO}_3$ , add 3–4 ml. of 20%  $\text{Pb}(\text{NO}_3)_2$  solution, followed by 2 grams of solid ammonium acetate. Stir well, filter and wash with hot water.

**Residue.** May contain  $\text{PbCrO}_4$  and  $\text{Pb}_3(\text{VO}_4)_2$  (4).

Dissolve in the minimum volume of hot 3N  $\text{HNO}_3$  (ca. 5–6 ml.), thoroughly cool the resulting solution, and transfer to a small separatory funnel. Add an equal volume of amyl alcohol, and a little 6%  $\text{H}_2\text{O}_2$ . Shake well and allow the two layers to separate.

A blue coloration in the upper layer indicates **Cr present**, and a red to brownish-red coloration (5) in the lower layer indicates **V present**.

Confirm V by the  $\text{KClO}_3$ -p-phenetidine test (Section IX, 11, reaction 12).

**Filtrate.** May contain  $\text{Al}(\text{NO}_3)_3$ ,  $\text{UO}_2(\text{NO}_3)_2$  and excess of  $\text{Pb}(\text{NO}_3)_2$ . Pass  $\text{H}_2\text{S}$  to remove all the Pb as  $\text{PbS}$ . Filter, wash and boil the filtrate to expel  $\text{H}_2\text{S}$ . Almost neutralise with  $\text{NH}_3$  solution, cool and pour into an excess of concentrated  $(\text{NH}_4)_2\text{CO}_3$  solution. Warm for 5 minutes. Allow to stand, filter and wash.

**Residue.**

White:

$\text{Al}(\text{OH})_3$ .

**Al present.**

Confirm by Thenard's blue test (6).

**Filtrate.** May

contain U, probably as  $(\text{NH}_4)_4[\text{UO}_2(\text{CO}_3)_2]$ .

Evaporate to a small volume (7), acidify with HCl, and add  $\text{K}_4[\text{Fe}(\text{CN})_6]$  solution. Brown ppt. of  $(\text{UO}_2)_2[\text{Fe}(\text{CN})_6]_3$ , becoming yellow upon the addition of NaOH solution.

**U present.**

*Notes.* (1) The potassium ferrocyanide test is not recommended here when U is present. The  $\text{NaOH-H}_2\text{O}_2$  separation is not quite quantitative and sufficient U may be present in the precipitate to introduce complications.

(2) The addition of phosphoric acid or of sodium phosphate is essential if Zr is to be tested for, even if Fe is absent (compare Section IX, 14, reaction 3).

(3) If both Ti and Zr are present, the ppt. of zirconium phosphate may be filtered off (best in the presence of a little macerated filter paper, or a Whatman filtration accelerator), and the filtrate treated with  $\text{Na}_2\text{SO}_3$  or with  $\text{Na}_2\text{S}_2\text{O}_3$  solution and warmed. The so-called "titanium peroxide" is reduced and titanium phosphate precipitates. It may be necessary to reduce the acidity of the solution somewhat to completely precipitate the titanium. Zr may also be identified by the alizarin-S reaction.

(4) If Group IV metals are present, they may be precipitated as vanadates. This is prevented by adding excess of  $\text{FeCl}_3$  solution when ferric vanadate is precipitated here.

(5) If much Cr and a little V is present, a second extraction with amyl alcohol may be necessary in order to ensure the complete removal of the Cr, and to render the coloration due to V completely visible. The addition of two drops of concentrated nitric acid intensifies the colour.

(6) The dry test is preferable to the "aluminon" reaction, for the latter is not applicable in the presence of Be. If Be is absent, the "aluminon" test may be applied.

(7) A precipitate that separates here may be (basic) beryllium carbonate. It should be filtered off and tested for Be by the basic acetate-chloroform test or by the acetylacetone test (see Section IX, 12, reactions 6 and 9).

### IX, 19. Notes on the Precipitation and Separation of Group IIIB in the presence of "Rarer" Elements

If thallium has been found in Group I, some of it may pass into Group IIIB because of the solubility of thallous chloride in water and be precipitated as  $\text{Tl}_2\text{S}$ . It may be readily detected by the green flame coloration, preferably viewed through a hand spectroscope. Thallium is best separated from the other elements of Group IIIB by dissolving the precipitate in dilute nitric acid, boiling to expel hydrogen sulphide, adding a little sulphurous acid solution and boiling again to remove excess of sulphur dioxide. Upon pouring the solution into excess of aqueous sodium carbonate, the carbonates of cobalt, nickel, manganese and zinc are precipitated and the thallium remains in solution as the soluble thallous carbonate. The precipitated carbonates may be dissolved in dilute hydrochloric acid and the usual separation carried out. The thallium in the filtrate can be precipitated by the addition of freshly prepared, colourless ammonium sulphide solution.

If vanadium and/or molybdenum have been detected in the earlier groups (as indicated by the production of a blue coloration

with hydrogen sulphide in acid solution), these elements may also be found in the filtrate from Group IIIB: a violet-red colour points to vanadium and a reddish-brown coloration to molybdenum. As a general rule, vanadium is generally removed in Group IIIA as iron vanadate and its presence in the Group IIIB filtrate is therefore unlikely. However, when the filtrate from Group IIIB is acidified with acetic acid and boiled, the production of a brown precipitate will indicate the removal of any residual molybdenum, vanadium or nickel in the form of sulphides. If desired, the precipitate may be dissolved in concentrated nitric acid, evaporated to dryness and the residue dissolved in hydrochloric acid. Molybdenum is detected by the ammonium thiocyanate or the potassium xanthate test (Section IX, 4), and vanadium by the  $\text{KClO}_3$ -*p*-phenetidine or hydrogen peroxide reactions (Section IX, 11).

#### LITHIUM, Li

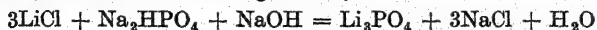
Lithium is a silver-white metal; it is the lightest metal known (density 0.534 at 0°) and floats upon petroleum. It oxidises on exposure to air, and reacts with water forming lithium hydroxide and liberating hydrogen, but the reaction is not so vigorous as with sodium and potassium. The metal dissolves in acids with the formation of salts. The salts may be regarded as derived from the monoxide  $\text{Li}_2\text{O}$ .

Some of the salts, notably the chloride  $\text{LiCl}$  and the chlorate  $\text{LiClO}_3$ , are very deliquescent. The solubilities of the hydroxide  $\text{LiOH}$  (113 grams per litre at 10°), carbonate  $\text{Li}_2\text{CO}_3$  (13.1 grams per litre at 13°), the phosphate  $\text{Li}_3\text{PO}_4$  (0.30 grams per litre at 25°) and the fluoride  $\text{LiF}$  (2.7 grams per litre at 18°) are less than the corresponding sodium and potassium salts, and in this respect lithium resembles the alkaline earth metals.

### IX, 20. REACTIONS OF LITHIUM COMPOUNDS

Use lithium carbonate  $\text{Li}_2\text{CO}_3$  dissolved in the minimum volume of 2*N* hydrochloric acid.

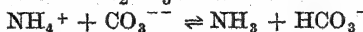
**1. Sodium Phosphate Solution:** partial precipitation of lithium phosphate  $\text{Li}_3\text{PO}_4$  in neutral solutions; the precipitate is more readily obtained from dilute solutions on boiling. Precipitation is almost complete in the presence of sodium hydroxide solution. The precipitate is more soluble in ammonium chloride solution than in water (distinction from magnesium).



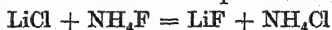
Upon boiling the precipitate with barium hydroxide solution, it passes into solution as lithium hydroxide (difference from magnesium).

**2. Sodium or Ammonium Carbonate Solution:** white precipitate of lithium carbonate  $\text{Li}_2\text{CO}_3$  from concentrated solutions and in the presence of ammonia solution. No precipitation occurs in the presence of high concentrations of ammonium chloride since

the carbonate ion concentration is reduced to such an extent that the solubility product of  $\text{Li}_2\text{CO}_3$  is not exceeded:



**3. Ammonium Fluoride Solution:** a white, gelatinous precipitate of lithium fluoride  $\text{LiF}$  is slowly formed in ammoniacal solution (distinction from sodium and potassium).



**4. Tartaric Acid, Sodium Cobaltinitrite or Chloroplatinic Acid Solution:** no precipitate (distinction from potassium). A precipitate of lithium cobaltinitrite is, however, produced in very concentrated (almost saturated) solutions of lithium salts; interference with the sodium cobaltinitrite test for  $\text{K}^+$  is therefore unlikely.

†5. **"Ferric Periodate" Test.**—Ferric salts react with periodates to yield a precipitate of a complex ferric periodate: this precipitate is soluble in excess of the periodate solution and also in excess of potassium hydroxide solution. The resulting alkaline solution of the ferric periodate complex is a selective reagent for lithium, since it gives a white precipitate  $\text{KLiFe}[\text{IO}_6]$ , even from dilute solutions and in the cold. Sodium and potassium give no precipitate: ammonium salts, all metals of Groups I to IV and magnesium should be absent.

Place a drop of the neutral or alkaline test solution in a micro test-tube, add 1 drop of saturated sodium chloride solution and 2 drops of the ferric periodate reagent. Carry out a blank test with a drop of distilled water simultaneously. Immerse both tubes for 15–20 seconds in water at 40–50°C. A white (or yellowish-white) precipitate indicates the presence of lithium; the blank remains clear.

Sensitivity: 0.1  $\mu\text{g}$ . Li. Concentration limit: 1 in 100,000.

The "ferric periodate" reagent is prepared by dissolving 2 grams of potassium periodate ( $\text{KIO}_4$ ) in 10 ml. of freshly prepared 2N potassium hydroxide solution, diluting with water to 50 ml., adding 3 ml. of 10 per cent ferric chloride solution and diluting to 100 ml. with 2N potassium hydroxide solution. The reagent is stable.

†6. **Ammonium Carbonate Solution (Microscope Test).**—Lithium carbonate, when freshly formed, has a characteristic appearance under the microscope.

Place a drop of the concentrated test solution on a microscope slide. Introduce a few minute specks of sodium or ammonium carbonate. Some lithium carbonate crystals are formed immediately. Examine under the microscope (magnification; *ca.* 200 diameters): the crystals are in the form of either hexagonal stars or plates (compare  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , Section III, 31, reaction 10).

The cations of the alkaline earth metals and of magnesium must be absent.

Concentration limit: 1 in 10,000.

### Dry Test

**Flame coloration.**—Lithium compounds impart a carmine-red colour to the non-luminous Bunsen flame. The colour is masked by the presence of considerable amounts of sodium salts, but becomes visible when observed through two thicknesses of cobalt glass.



The most distinctive test utilises the spectroscope; the spectrum consists of a beautiful red line at 6708Å.

To separate lithium from the other alkali metals, they are all converted into the chlorides (by evaporation with concentrated hydrochloric acid, if necessary), evaporated to dryness, and the residue extracted with absolute alcohol which dissolves the lithium chloride only. Better solvents are dry dioxan (diethylene dioxide,

$\text{O} \begin{pmatrix} \text{CH}_2.\text{CH}_2 \\ \text{CH}_2.\text{CH}_2 \end{pmatrix} \text{O}$ ) and dry acetone. Upon evaporation of the

extract, the residue of lithium chloride is (a) subjected to the flame test, and (b) precipitated as the phosphate after dissolution in water and adding sodium hydroxide solution.

#### Note on the Detection of Lithium in Group V

This element is readily detected in the residue of Group V by means of the hand spectroscope (see Section II, 1, 4). Details for the separation of Li from K and Na are given in the previous paragraph.

In Table VI are collected the colorations produced with the borax beads for difference elements and will be useful for reference purposes (compare Section VII, 2, test (iv)).

#### IX, 21

Table VI. Borax Bead Tests

<i>Oxidising flame</i>		<i>Reducing flame</i>		<i>Metal</i>
<i>Hot</i>	<i>Cold</i>	<i>Hot</i>	<i>Cold</i>	
1. Green	Blue	Colourless	Opaque red or brown*	Copper
2. Yellowish-brown	Yellow	Green	Green	Iron
3. Yellow	Green	Green	Green	Chromium
4. Violet (amethyst)	Amethyst	Colourless	Colourless	Manganese
5. Blue	Blue	Blue	Blue	Cobalt
6. Violet	Reddish-brown	Grey	Grey	Nickel
7. Yellow	Colourless	Brown	Brown	Molybdenum
8. Rose-violet	Rose-violet	Red	Violet	Gold
9. Yellow	Colourless	Yellow	Yellow-brown	Tungsten†
10. Yellow	Pale yellow	Green	Bottle-green	Uranium
11. Yellow	Greenish-yellow	Brownish	Emerald-green	Vanadium
12. Yellow	Colourless	Grey	Pale-violet	Titanium‡
13. Orange-red	Colourless	Colourless	Colourless	Cerium

\* Bright red in the presence of a trace of tin.

† Microcosmic salt bead test: reducing flame, cold—blue; blood-red when fused with a trace of ferrous sulphate.

‡ Microcosmic salt bead test: reducing flame, hot—yellow, cold—violet; blood-red with a trace of ferrous sulphate.

## CHAPTER X

### PAPER CHROMATOGRAPHY

**X, 1. Introduction.  $R_F$  Values.**—In filter-paper chromatography a small amount of material (say, an aqueous solution containing a mixture of cations) is placed upon a limited area near the end of a strip of filter paper, and a solvent is allowed to diffuse from the end of the paper by capillary action: under suitable conditions and after some time (1–30 hours), the mixture will be found to have migrated from its limited area of application and separated wholly or partially into its components as distinct zones. The zones in the form of spots or bands may be located by the application of appropriate chemical reagents to the paper or by ultra-violet fluorescence. The diffusion of the solvent and the resulting separation into spots or bands is sometimes termed the development of the chromatogram; this term is a little misleading and should not be confused when employed in the above sense with the subsequent identification process by means of which the zones are rendered clearly visible by treatment of the paper with various reagents. The author prefers to confine the phrase “development of the chromatogram” to signify the treatment of the chromatogram *after* it has been formed, and it will have this significance when employed in the present chapter.

To specify the position attained by a substance or ion in a paper chromatogram, the term  $R_F$  was introduced: this is the ratio of the distance travelled by the substance or ion to that of the solvent front, measured from the point of application of the mixture. Fig. X, 1, will help to make the definition of  $R_F$  clear: in (a) the strip of filter paper is shown immersed in the solvent and supported by a glass rod; in (b) AB indicates where the spot of the solution was applied at the beginning of the experiment; in (c) the position of two bands (rendered visible, for example, by spraying with an appropriate chemical reagent) C and D, and also of the solvent front E, are indicated. The  $R_F$  value for the substance or ion at C is  $x/z$  and the substance or ion at D is  $y/z$ . It is found that under comparable conditions many ions have characteristic  $R_F$  values; separation by paper chromatography is usually possible when the  $R_F$  values differ by about 0.1.

The position of AB (usually a pencilled line) is fixed by applying a drop of the solution from a capillary pipette or micro syringe along the line. The distance moved by the substance or ion is generally taken as the distance between the line AB and the "centre of gravity" of the band; the resulting  $R_F$  value does not take into account the width of the band and also some uncertainty may be introduced if the band has diffuse boundaries.

The values of  $R_F$  are reasonably constant providing close control of all variables is maintained. It is found, however, that the relative rates of movement are constant with less

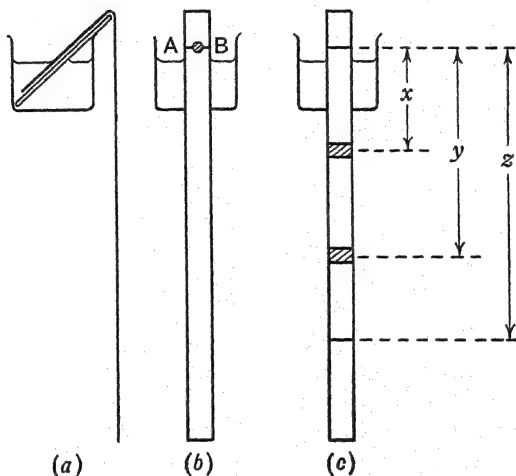


Fig. X, 1, 1

rigid control, thus enabling one band on a strip to be identified by its position relative to known bands. Furthermore, with the large number of "spot" tests available for the detection of individual inorganic radicals, the necessity for an accurate knowledge of  $R_F$  values is diminished. If constancy of pure solvents, of temperature and saturation of the atmosphere are maintained, it is found that  $R_F$  values are influenced *inter alia* by the following factors:

(a) The presence of other ions, *e.g.* the presence of chloride in separations carried out with nitrate solutions.

(b) The acidity of the original solution: this may be due to the need for acid in the formation of a complex which is soluble in the organic solvent, to prevent hydrolysis of the salt, etc.

(c) The time of running of a strip; sometimes the  $R_F$  values increase with the time of running at the outset and this may correspond with a decrease in the rate of movement of the solvent front.

(d) The presence and concentration of other cations.

It is not proposed to deal with the theory of paper chromatography here, but it may be pointed out that an important factor is the distribution of the inorganic compound between an organic solvent and water. The distribution may be varied *inter alia* by forming complexes of the cations with different organic solvents or mixtures of solvents.

The separation of metals constituting the usual groups in qualitative analysis, and also the isolation of the constituents of mixtures containing some of the less common metals, will be described. A few separations of anions will also be given in outline.

Some advantages of paper chromatography may be mentioned:

- (i) The procedure is simple and reasonably rapid.
- (ii) Costly special apparatus and reagents are not necessary.
- (iii) Only small quantities of materials are required.
- (iv) The method has proved successful for the separation and detection of groups of metals which are difficult to deal with by routine qualitative analysis, *e.g.* the separation of the platinum metals from one another, of beryllium from aluminium, of scandium from the rare earths and thorium, and of hafnium from zirconium.

**X, 2. Apparatus and General Technique.**—For general use, Whatman No. 1 paper is satisfactory. No. 3MM is similar in speed but thicker, and therefore has a higher water content. Whatman No. 4 is a very much "faster" paper; it is not widely employed in inorganic chromatography.

For routine work in qualitative analysis, the apparatus depicted in Fig. X, 2, 1 is inexpensive and efficient. It consists of a glass gas jar or measuring cylinder (say, 22 inches by 3 inches), closed with a tight-fitting cork or rubber bung which carries a glass rod to which a glass boat is fused. (The glass boat, with approximate dimensions, is shown in Fig. X, 2, 2.) The boat is suspended about an inch below the bottom of the cork, and serves as a container for the solvent employed in the separations. Two side arms are fused to the glass rod above the glass boat and these act as supports for a pair of paper strips; only one paper strip is shown in position in the

diagram. In order to saturate the atmosphere in the cylinder with respect to the solvent, a layer of the latter is kept at the bottom of the glass cylinder; this will prevent evaporation effects from disturbing the equilibrium of the solvents traveling down the paper. In some separations it is also necessary to control the amount of water vapour in the atmosphere; for this purpose a beaker containing water, saturated salt solution or aqueous acid saturated with the solvent is placed on the bottom of the jar. It is advantageous to maintain fairly constant temperature conditions and for some separations the whole apparatus is kept in a thermostatically controlled ( $\pm 1^\circ$ ) cabinet or bath. The size of the airtight container should be commensurate with the narrow strips of filter paper

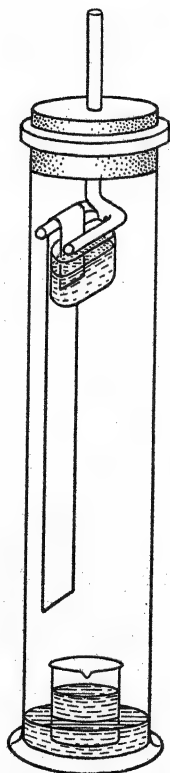


Fig. X, 2, 1

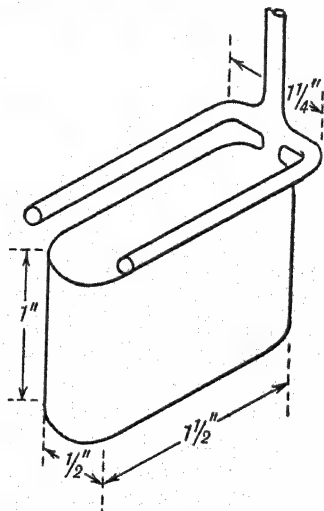


Fig. X, 2, 2

ordinarily employed, otherwise with volatile solvents it is difficult to maintain the equilibrium of the solvent mixture running in the paper and which is essential for the separation.

The procedure permits the separation of 1-200  $\mu\text{g.}$  of ions: under favourable conditions as much as 1 mg. (1000  $\mu\text{g.}$ ) of certain ions may be separated by chromatography. Strips of Whatman No. 1 filter paper, 12-18 inches long and 1 inch wide, are cut from the rolls supplied by the manufacturers.

A light pencil line is drawn across the width of the paper about 3 inches from the upper edge; this acts as the zero line. A convenient volume (say, 0.05 ml.) of the test solution, containing not more than 1 mg. of the mixed metals (say, as chlorides) is applied to the centre of the zero line with the aid of a micro pipette\*: the strip is held horizontally until the liquid is absorbed. The spot usually forms a wet patch about one inch square; this is generally allowed to dry completely in the air (*ca.* one hour), although in some cases the degree of drying is dependent upon the chemical stability of the salts undergoing separation. The strip is then hung vertically in the cylinder with the upper end immersed in the solvent contained in the glass boat; the upper end of the strip may be held down in the glass boat by means of a glass rod, but with two strips touching in the trough, the capillary and other forces suffice to hold the strips in position without the necessity of weighting. After the solvent has diffused down the paper a sufficient distance to effect a separation (1–24 hours; this may be when the solvent front has travelled within 1–2 inches of the lower edge of the paper), the strip is removed from the cylinder. The position of the solvent front should be marked whilst the strip is still wet with solvent, since it is sometimes difficult to locate it when dry.† The solvent is then allowed to evaporate, *i.e.* the strips are dried by pinning or clipping them over a glass rod clamped or supported at a convenient height. The presence and position of the salts on the strip are detected by spraying with a suitable reagent. The simple type of atomiser shown in Fig. II, 6, 5, inserted in a test-tube or small flask, may be used. [If available, it is more satisfactory to employ a commercial form of atomiser operated by a constant pressure device (*ca.* 10 lb./sq. in.).] After spraying, the coloured bands may not reach their maximum intensity until several hours have elapsed.

A large number of organic and inorganic reagents have been used. The criteria applied in selecting a reagent for paper chromatography differ from those usually employed in choosing a "spot" test reagent. It is not necessary for the reagent to

\* It has been recommended that a series of micro drops (say, from a micro syringe of the Burroughs Wellcome type) be placed at intervals along the pencil line: this procedure is not essential for routine work in qualitative inorganic analysis.

† For some mixed solvents containing water, there may be two solvent fronts, one of the dry solvent (lower area—the position of this is noted) and another wet solvent front (upper area, in which the paper is saturated with water).

be specific for a certain ion or radical, but it is desirable to have one which will give a test for as many ions or radicals as possible. The reagents employed include diphenylthiocarbazone (dithizone), rubeanic acid, diphenylcarbazide, alizarin, salicylaldehyde, morin, potassium ferrocyanide, potassium chromate, ammonium sulphide and hydrogen sulphide (as the free gas). In many instances mixtures of two or more of these reagents are advantageous.

In order to obtain repeatable results, the compositions of the solvents employed must be constant. In some cases, particularly with water-miscible solvents, small variations in the water content may affect considerably the efficiency of the separation. All the solvents used must be of high purity.

Some of the solvents employed are detailed below:

(i) *n*-Butyl alcohol saturated with 3*N* hydrochloric acid. Equal volumes of the alcohol and 3*N* hydrochloric acid are shaken together; the upper layer is used.

(ii) Acetylacetone is saturated with water: to 7.5 ml. of the saturated solvent, 0.05 ml. of concentrated hydrochloric acid and 2.5 ml. of dry acetone are added. This solvent is described as acetylacetone saturated with water and containing 0.5 per cent (v/v) of hydrochloric acid (*d* 1.18) and 25 per cent (v/v) of dry acetone.

(iii) Glacial acetic acid containing 25 per cent (v/v) of dry methyl alcohol.

(iv) Acetone containing 5 per cent (v/v) of water and 8 per cent (v/v) of hydrochloric acid (*d* 1.18).

(v) Pyridine containing 20 per cent (v/v) of water and 1 per cent (w/v) of potassium thiocyanate.

(vi) Methyl alcohol.

(vii) Methyl ethyl ketone containing 30 per cent (v/v) of hydrochloric acid (*d* 1.18).

(viii) Cellosolve (ethylene glycol monoethyl ether) containing 20 per cent (v/v) of hydrochloric acid (*d* 1.18).

(ix) Ethyl ether containing 2 per cent (w/v) of dry hydrogen chloride and 7.5 per cent (v/v) of dry methyl alcohol.

(x) Methyl acetate containing 3 per cent (v/v) of methyl alcohol and 10 per cent (v/v) of water.

(xi) Dry *n*-butyl alcohol containing 40 per cent (v/v) of dry methyl alcohol.

(xii) Tetrahydrosulvan containing 5 per cent (v/v) of water and 10 per cent (v/v) of nitric acid (*d* 1.42).

(xiii) Pyridine containing 10 per cent (v/v) of water.

The following details for the **purification of solvents for paper chromatography** may be useful:

**Acetone.** Reflux with solid potassium hydroxide and potassium permanganate for one hour, and fractionate. Use the fraction, b.p.  $56^{\circ} \pm 0.5^{\circ}$ .

**Methyl ethyl ketone.** As for acetone. Use fraction, b.p.  $79.5-80^{\circ}$ .

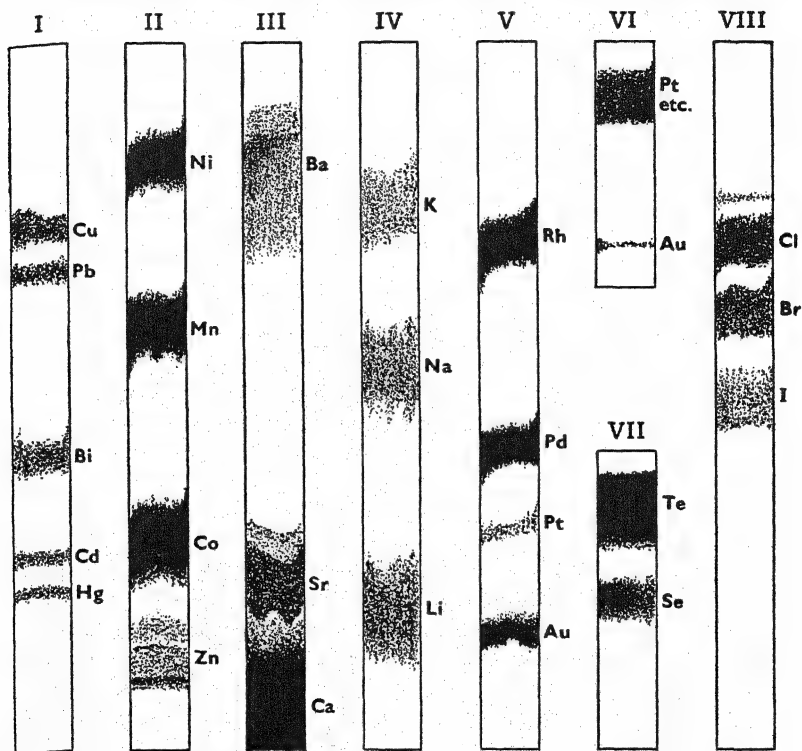


Fig. X, 2, 3

**Methyl n-propyl ketone.** As for acetone. Use fraction, b.p.  $99-102^{\circ}$ .

**Methyl alcohol.** Redistil the purest commercial (synthetic) alcohol. B.p.  $63^{\circ}$ .

**n-Butyl alcohol.** Dry over anhydrous calcium sulphate, filter and distil. Use fraction, b.p.  $116.5-117.5^{\circ}$ .

**Pyridine.** The AnalaR brand is satisfactory.

**Ethyl acetate.** Shake with saturated calcium chloride solution, dry with anhydrous calcium sulphate, filter and distil. B.p.  $76.5-77.5^{\circ}$ .



*Methyl acetate.* As for ethyl acetate. B.p. 56.5–57.5°.

*Diethyl ether.* Reflux with alkaline potassium permanganate, dry with anhydrous calcium sulphate, filter and distil. B.p. 35°. The ether is free from peroxides.

*Tetrahydrofuran.* As for diethyl ether. B.p. 79–80°.

The results of some typical separations are shown in Fig. X, 2, 3; the Figure has been drawn from actual photographs of the paper chromatograms. The following separations are indicated:

I—Group IIA, Cu, Pb, Bi, Cd and Hg.

II—Group IIIB, Ni, Mn, Co and Zn.

III—Group IV, Ba, Sr and Ca.

IV—K, Na and Li.

V—Rh, Pd, Pt and Au.

VI—Au from the Pt metals.

VII—Te and Se.

VIII—Cl, Br and I.

Full details of these separations are given in the following Sections.

### X, 3. SOME TYPICAL GROUP SEPARATIONS

**Group I.—Ag, Pb and Hg (ous).** The metals are present as nitrates in dilute nitric acid. The solution is spotted upon paper and allowed to dry in air for one hour. The solvent consists of *n*-butyl alcohol, mixed with 5 per cent (v/v) of glacial acetic acid, followed by water to turbidity. The separation (elution) is allowed to proceed for 12–16 hours in an atmosphere saturated with the solvent. The strip is removed from the extraction vessel, dried in air and then sprayed with a 0.05 per cent solution of dithizone in chloroform.

	<i>R<sub>F</sub></i> values	Colour of band
Pb	0.08	Rose pink.
Ag	0.16	Orange.
Hg (ous)	0.85	Pink.

The paper chromatogram may also be developed by exposure to hydrogen sulphide gas, but the results are not as satisfactory as with dithizone.

**Group IIA.—Hg, Pb, Bi, Cu and Cd.** The metals are present as chlorides in dilute hydrochloric acid. The solvent

used is *n*-butyl alcohol saturated with 3*N* hydrochloric acid. To obtain a good separation of copper and lead, the strip should be at least 18 inches long. The solvent is allowed to flow for 15–18 hours in an atmosphere saturated with respect to both organic solvent and aqueous phases. After evaporation of the solvent, the strip is sprayed with a solution of dithizone in chloroform (0.05 per cent w/v). Lead gives only a weak colour with dithizone and is best detected by spraying the top portion of the strip with an aqueous solution of rhodizonic acid.

	<i>R<sub>F</sub></i> values	Reagent	Colour of band
Cu	0.20	Dithizone	Purple-brown.
Pb	0.27	Rhodizonic acid	Bright blue.
Bi	0.59	Dithizone	Purple.
Cd	0.77	Dithizone	Purple.
Hg (ic)	0.81	Dithizone	Pink.

**Group IIB.—As, Sb and Sn.** The separation of a mixture of the three elements is a difficult operation. The metals are present as their lower chlorides in dilute (2–4*N*) hydrochloric acid. The solution is spotted on paper and allowed to dry in air for 15 minutes. The solvent consists of 7.5 ml. of acetylacetone (b.p. 137–141°) saturated with water and treated with 0.05 ml. of concentrated hydrochloric acid and 2.5 ml. of acetone (sufficient of the last-named to give a clear solution). The separation is allowed to proceed for 1 hour in an atmosphere saturated with respect to a saturated solution of acetylacetone in water; the solvent movement is about 15 cm. The complexes formed are very stable, particularly that with tin ( $R_F = 1$ ). The strip is removed from the extraction vessel, the solvent is allowed to evaporate for several minutes, and the strip is sprayed (before it is completely dry) with a chloroform solution of dithizone (0.05 per cent w/v), and then allowed to dry thoroughly. The tin is found in the solvent front.

	<i>R<sub>F</sub></i> values	Colour of band
As	0.2	Yellow.
Sb	0.5	Red.
Sn	1.0	Purple.

**Group IIIA.—Fe, Al and Cr.** The main difficulty here is the separation of the aluminium and chromium. The metals are present as chlorides in 5*N* hydrochloric acid. The solvent employed is glacial acetic acid containing 25 per cent (v/v) of dry methyl alcohol. The test solution is spotted upon filter paper and allowed to evaporate to dryness in air. The elution is allowed to proceed for 12 hours in an atmosphere saturated with respect to the mixed solvents: the use of a saturated solution of potassium carbonate to maintain a low humidity improves the separation. After the solvent has evaporated, the strip is cut lengthwise in two portions. One portion is sprayed with a saturated alcoholic solution of alizarin, made alkaline by exposure to ammonia vapour and then warmed; Al appears as a red band well separated from a purple band due to iron. The other portion of the strip is sprayed first with 5 per cent aqueous sodium peroxide and then with a 0.05 per cent solution of benzidine in 10 per cent acetic acid: Cr is indicated as a bright blue band just behind the Al.

**Group IIIB.—Ni, Co, Mn and Zn.** The metals are present as chlorides in dilute hydrochloric acid. The solvent used is acetone containing 5 per cent (v/v) of water and 8 per cent (v/v) of hydrochloric acid ( $d$  1.18). The separation is conducted in an atmosphere saturated with respect to the solvent. The strip is dried (after a solvent movement of about 25 cm.), exposed to ammonia vapour and then sprayed with a saturated alcoholic solution of alizarin containing 0.1 per cent of rubeanic acid and 1 per cent salicylaldehyde. The following results are obtained.

	<i>R<sub>F</sub></i> values	Colour of band
Ni	0.07	Blue.
Mn	0.3	Brown.
Co	0.6	Brown.
Zn	0.9	Purple.

**Group IV.—Ca, Sr and Ba.** This is a difficult separation. The metals are present as chlorides. The solvent used is pyridine containing 20 per cent (v/v) of water and 1 per cent (w/v) of potassium thiocyanate. The elution is allowed to proceed for 5–6 hours in an atmosphere saturated with respect to pyridine and also with a relative humidity of between 65 and 80 per cent; the latter is attained by the use of a saturated

aqueous solution of ammonium nitrate or chloride. The solvent front moves about 20 cm. The strip is dried, and then sprayed with a saturated alcoholic solution of alizarin to identify Ca, and with 0.1 per cent (w/v) aqueous sodium rhodizonate (freshly prepared) to reveal Ba and Sr. The  $R_F$  values are: Ca, 0.95; Sr, 0.75; Ba, 0.15.

**Group V.—Na, K and Li.** The metals are present as chlorides in neutral solution. The solvent used is methyl alcohol. The position of the alkali metal chloride bands is detected by spraying with 0.1*N* silver nitrate and 0.1 per cent fluorescein in 50 per cent alcohol, and then drying the strip. The  $R_F$  values are: Li, 0.8; Na, 0.5; K, 0.1.

**Alkaline earth and alkali metals.—Be, Ca, Sr, Ba, Mg; Na, K and Li.** The experimental details given below permit the separation of Be, Mg, Ca, Sr and Ba; Mg, Na and K; Mg, Ca, Na and K; and of Li, Na and K. The metals are present as acetates in dilute acetic acid solution. The solvent is a mixture of 80 per cent ethyl alcohol and 20 per cent (v/v) of 2*N* acetic acid. The elution is allowed to proceed for about 24 hours. The paper chromatogram, after drying in an air oven at 60°C, is developed by spraying with 0.1 molar aqueous solution of violuric acid (5-isonitroso-barbituric acid) and then dried at 60°C. The  $R_F$  values and the colours of the bands are collected below.

<i>Metal</i>	<i>R<sub>F</sub> values</i>	<i>Colour of band</i>
Be	0.86	Yellowish-green.
Mg	0.76	Yellowish-red.
Ca	0.68	Orange.
Sr	0.55	Reddish-violet.
Ba	0.43	Pale red.
Li	0.76	Reddish-violet.
Na	0.56	Reddish-violet.
K	0.45	Violet.

The reagent (obtainable from Eastman Kodak, etc.) is expensive.

**Separation of Halides.—F, Cl, Br and I.** The anions are present as their sodium salts. The solvent used is either

pyridine containing 10 per cent (v/v) of water, or acetone containing 20 per cent (v/v) of water. The elution is conducted during 1.5–2 hours in an atmosphere saturated with solvent vapour. After evaporation of the solvent from the strip, the latter is cut longitudinally. One part is sprayed with 0.1*N* silver nitrate and 0.1 per cent fluorescein in 50 per cent alcohol, and the other is sprayed with the zirconium–alizarin reagent. Upon drying, the halides are clearly visible as characteristic bands, which when viewed under ultra-violet light appear as dark areas on a fluorescent background. The  $R_F$  values are as follows.

Radical	Pyridine—10% $H_2O$	Acetone—20% $H_2O$
Fluoride	0.00	0.25
Chloride	0.24	0.51
Bromide	0.47	0.62
Iodide	0.71	0.77

**Separations of Various Anions.** Using a solvent mixture composed of *n*-butyl alcohol, pyridine and 1.5*N* ammonia solution in the proportions of 2 : 1 : 2, the following  $R_F$  values are obtained for the sodium or potassium salts: chloride, 0.24; bromide, 0.36, iodide, 0.47; chlorate, 0.42, bromate, 0.25, iodate, 0.09; nitrite, 0.25; nitrate, 0.40; arsenite, 0.19; arsenate, 0.05; phosphate, 0.04; and thiocyanate, 0.56. The positions of the anions may be detected by spraying with ammoniacal silver nitrate; potassium iodide and hydrochloric acid is particularly effective for chlorates, bromates and iodates. The  $R_F$  values provide the basis for the separation of a number of mixtures of anions, *e.g.* chloride and iodide, bromide or iodide and nitrate.

#### X, 4. MISCELLANEOUS SEPARATIONS

A number of interesting and, in some cases, difficult separations have been achieved by paper chromatography and details of some of these are given below. They serve to emphasise the great value of the technique.

**Aluminium and Beryllium.** The metals are present as chlorides in dilute hydrochloric acid. The solvent consists of 80 per cent *n*-butyl alcohol and 20 per cent hydrochloric acid. After elution overnight, the solvent front moves about 20 cm.

The positions of the aluminium and beryllium bands are shown by spraying with an alcoholic solution of 8-hydroxyquinoline. The bands fluoresce under ultra-violet light; the fluorescence intensifies upon drying the paper and exposing to ammonia gas. The  $R_f$  values are: Al, 0.03; Be, about 0.3.

This procedure permits the detection of 2  $\mu\text{g.}$  of Al in the presence of 300  $\mu\text{g.}$  of Be, and *vice versa*; traces of Be can thus be detected in Al salts and traces of Al in Be salts.

**Separation of Mercury from other Metals.** The procedure enables 1  $\mu\text{g.}$  of Hg to be identified in the presence of a large excess of Pb, Cu, Bi, Cd, As, Sb, Fe, Al, Cr, Ni, Co, Mn and Zn. The metals are present as chlorides. The solvent used is methyl acetate containing 3 per cent (v/v) of methyl alcohol and 10 per cent (v/v) of water.

The test solution should not contain more than 5 per cent (v/v) of concentrated hydrochloric acid and must have a  $\text{pH} < 2$ . It is spotted on a paper strip and allowed to evaporate for 10–15 minutes. Diffusion of the solvent takes place in an atmosphere saturated with respect to the vapour of a saturated solution of methyl acetate in water, and the temperature is maintained constant at  $22^\circ$ . The solvent moves sufficiently far in 20–30 minutes to effect a complete separation. After evaporation of the solvent, the strip is made alkaline by exposure to ammonia vapour and then sprayed with a 1 per cent solution of diphenylcarbazide in alcohol. Mercury is indicated by a narrow blue band in the dry solvent front.

**The Platinum Metals: Pt, Pd, Rh, Ir, Ru, Os and Au.** The metals are present as their chlorides or sodium chloro-salts. The solvent used is methyl ethyl ketone containing 30 per cent (v/v) of hydrochloric acid ( $d$  1.18); it is freshly prepared. The solution is spotted on the paper strip and allowed to dry thoroughly in the air. The atmosphere in the separation vessel is saturated with respect to the solvent. For the detection of Pt, Pd, Au and Rh, 0.5*N* stannous chloride in dilute hydrochloric acid is a suitable developing reagent; a mixture of stannous chloride and potassium iodide solution is somewhat more sensitive. Iridium is reduced to the colourless iridium trichloride by the stannous chloride, but can be re-oxidised to the brown tetrachloride by chlorine water. Ruthenium and osmium are detected by spraying with a solution of thiourea in 5*N* hydrochloric acid; warming is necessary to develop the colours fully.

The  $R_F$  values are: Ru, 0.08; Rh + Ir, 0.10; Pd, 0.60; Pt, 0.80; Au, 0.95. The separation of the four elements Rh, Pd, Pt and Au is comparatively easy.

**Gold from the Platinum Metals.** The metals are present as chlorides in hydrochloric acid (concentration  $> 2N$ ). The solvent is diethyl ether containing 2 per cent (w/v) of dry hydrogen chloride and 7.5 per cent (v/v) of dry methyl alcohol. The solution is spotted upon filter paper and the strip dried for one hour only. The separation is conducted in an atmosphere of solvent vapour. The solvent mixture extracts gold in a narrow band in the solvent front, while the platinum metals remain in the original spot; the developing reagent is 0.5*N* stannous chloride in dilute hydrochloric acid. It is easy to detect 1  $\mu$ g. of gold in the presence of more than 100 times the quantity of platinum metals.

**Selenium and Tellurium.** The elements are present as selenite and tellurite in dilute nitric acid solution. The mixture is spotted upon paper and dried thoroughly in the air. The solvent is dry *n*-butyl alcohol containing 4 per cent (v/v) of dry methyl alcohol. The atmosphere in the separation vessel is saturated with respect to the solvent vapour and the relative humidity is also maintained at 50 per cent by means of a saturated solution of calcium nitrate. The solvent is allowed to diffuse 8–10 cm. down the strip (*ca.* 2 hours). After evaporation of the solvent, the strip is sprayed with 0.5*N* stannous chloride in dilute hydrochloric acid. The tellurium is indicated by a black band ( $R_F$  0.1) and the selenium as an orange band ( $R_F$  0.5). It is possible to detect 1–5  $\mu$ g. of Se in the presence of 1 mg. of Te by this method.

**Scandium, Thorium and the Rare Earths.** The metals are present as nitrates in dilute nitric acid solution. The solvent is tetrahydrofuran containing 5 per cent (v/v) of water and 10 per cent (v/v) of nitric acid (*d* 1.42). The mixture is spotted upon paper and dried thoroughly in the air. The relative humidity inside the extraction vessel is maintained at 80 per cent by means of a saturated solution of ammonium chloride. After the solvent has diffused about 15 cm. down the solvent strip, it is allowed to evaporate, and the strip is placed for about 10 minutes in an atmosphere of ammonia vapour. The paper chromatogram is then sprayed with an alcoholic solution of alizarin and finally with *N* acetic acid. The following results are obtained.

	$R_F$	Colour of band
Th	0.96	Violet-blue.
Sc	0.17	Violet.
Rare earths	0.00	Violet-blue.

Scandium can also be separated from the rare earths by using methyl acetate containing 10 per cent (v/v) of water and 5 per cent (v/v) of nitric acid ( $d$  1.42) as solvent. The strip is subjected to a solvent run of 25 cm. Scandium is then found in a narrow strip ( $R_F$  0.17), but thorium forms a more diffuse band.

**Uranium in Mineral Ores.** An approximately 10 per cent solution of the sample containing 25–50 per cent of free nitric acid (by volume) is prepared by a suitable method (*e.g.* a potassium hydroxide or sodium peroxide fusion, followed by treatment with nitric acid). 0.05 ml. of the sample is spotted upon filter paper in the usual manner and allowed to dry in the air. The solvent consists of tetrahydro-sylvan (2-methyl tetrahydro-furan) saturated with water and to which sufficient concentrated nitric acid has been added to give a 2.5–10 per cent concentration of nitric acid. The paper strip is removed when the solvent front has moved 5–7 cms. beyond the test patch, and dried in a current of warm air. The uranium moves in a narrow band near the solvent front. The paper is sprayed with 1 per cent potassium ferrocyanide solution. A brown stain appears in the presence of uranium. The quantity of uranium may be estimated by comparison with standard stains prepared with known amounts (0.1–200  $\mu\text{g.}$ ) of uranium.

**Zirconium and Hafnium.** This separation must rank as one of the major achievements of inorganic paper chromatography. The metals are present as zirconyl and hafnyl nitrates; basic nitrates must be absent since these are immobile. The mixture is best prepared by digesting the sample at 80°C with concentrated nitric acid and evaporating the excess of acid at the same temperature under reduced pressure: the product gives a clear solution when dissolved in water.

The solvent is prepared by adding slowly 30 ml. of concentrated nitric acid ( $d$  1.42) to 70 ml. of dichlorotriethylene glycol; the mixture is stable for 2–3 days at room temperature. A total of 150  $\mu\text{g.}$  of mixed oxides can be handled with a Whatman No. 1 paper strip, 3 cm. wide. The solution (0.02 ml.) is



applied to the paper and, without drying, is immediately transferred to the extraction vessel. The chromatogram is allowed to run for 18 hours: the solvent moves about 3 cm. per hour, and drips from the end of the strip at the end of the period. The wet strip is sprayed with a saturated solution of alizarin in ethyl alcohol containing 5 per cent (v/v) of 2*N* hydrochloric acid. The strip is then heated gently, care being taken that it never becomes completely dry; it is resprayed with the reagent, if necessary. The characteristic red lines of the zirconium and hafnium lakes appear slowly against the yellow background of the reagent. Narrow bands are obtained with  $R_F$  values of 0.1 for Hf and 0.2 for Zr. It is possible to detect 2  $\mu$ g. of each metal, and also the presence of about 2 per cent of hafnium in commercial zirconium nitrate.

## APPENDIX

### A, 1.      ATOMIC WEIGHTS OF ELEMENTS (1952)

Aluminium, Al	26.98	Molybdenum, Mo	95.95
Antimony, Sb	121.76	Nickel, Ni	58.69
Argon, A	39.944	Niobium, Nb	92.91
Arsenic, As	74.91	Nitrogen, N	14.008
Barium, Ba	137.36	Osmium, Os	190.2
Beryllium, Be	9.013	Oxygen, O	16.000
Bismuth, Bi	209.00	Palladium, Pd	106.7
Boron, B	10.82	Phosphorus, P	30.975
Bromine, Br	79.916	Platinum, Pt	195.23
Cadmium, Cd	112.41	Potassium, K	39.100
Calcium, Ca	40.08	Radium, Ra	226.05
Carbon, C	12.010	Rhenium, Re	186.31
Cerium, Ce	140.13	Rhodium, Rh	102.91
Chlorine, Cl	35.457	Ruthenium, Ru	101.7
Chromium, Cr	52.01	Scandium, Sc	44.96
Cobalt, Co	58.94	Selenium, Se	78.96
Copper, Cu	63.54	Silicon, Si	28.09
Fluorine, F	19.00	Silver, Ag	107.880
Germanium, Ge	72.60	Sodium, Na	22.997
Gold, Au	197.2	Strontium, Sr	87.63
Hafnium, Hf	178.6	Sulphur, S	32.066
Helium, He	4.003	Tantalum, Ta	180.88
Hydrogen, H	1.008	Tellurium, Te	127.61
Iodine, I	126.91	Thallium, Tl	204.39
Iridium, Ir	193.1	Thorium, Th	232.12
Iron, Fe	55.85	Tin, Sn	118.70
Lanthanum, La	138.92	Titanium, Ti	47.90
Lead, Pb	207.21	Tungsten, W	183.92
Lithium, Li	6.940	Uranium, U	238.07
Magnesium, Mg	24.32	Vanadium, V	50.95
Manganese, Mn	54.93	Zinc, Zn	65.38
Mercury, Hg	200.61	Zirconium, Zr	91.22

## A, 2.

## REAGENTS

## CONCENTRATED ACIDS

	<i>Specific gravity</i>	<i>Per cent by weight</i>	<i>Approximate normality</i>
Acetic acid, glacial	1.05	99.5	17N
Hydrobromic acid	1.49	48	9N
Hydrochloric acid	1.19	38	12N
Hydrofluoric acid		48	27N
Hydriodic acid	1.70	57	7N
Nitric acid	1.42	70	16N
Perchloric acid	1.54	60	9N
Phosphoric acid	1.69	85	45N
Sulphuric acid	1.84	96	36N

## DILUTED ACIDS

	<i>Approximate normality</i>
<b>Acetic acid.</b> —Dilute 285 ml. of the concentrated acid to 1 litre with water ... ..	5N
<b>Hydrochloric acid.</b> —Dilute 430 ml. of the concentrated acid to 1 litre with water ... ..	5N
<b>Nitric acid.</b> —Dilute 310 ml. of the concentrated acid to 1 litre with water ... ..	5N
<b>Sulphuric acid.</b> —Pour 140 ml. of the concentrated acid slowly and with constant stirring into 500 ml. of water, cool, and dilute to 1 litre ...	5N
<b>Sulphurous acid.</b> —Prepare a saturated solution in water (6-7 per cent by weight) ... ..	0.3N

## BASES

<b>Ammonia solution, concentrated.</b> —The commercial product, sp. gr. 0.88, contains about 28 per cent $\text{NH}_3$ ... ..	15N
<b>Ammonia solution, dilute.</b> —Dilute 335 ml. of the concentrated solution to 1 litre with water ...	5N
<b>Barium hydroxide solution.</b> —Shake 70 grams of crystallised barium hydroxide $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ with 1 litre of water; filter or siphon off the liquid (saturated solution) and protect from $\text{CO}_2$ of the air ... ..	0.4N

Approximate  
normality

**Calcium hydroxide solution.**—Shake 2-3 grams of calcium hydroxide with 1 litre of water; filter or siphon off the liquid (saturated solution) and protect from  $\text{CO}_2$  of the air ... .. 0.04N

**Potassium hydroxide solution.**—Dissolve 125 grams of the ordinary "pure" sticks (about 90 per cent KOH) or, better, pellets in water and dilute to 1 litre ... .. 2N

**Sodium hydroxide solution.**—Dissolve 220 grams of the ordinary "pure" sticks (about 90 per cent NaOH) or, better, pellets in water and dilute to 1 litre ... .. 5N

## SALT SOLUTIONS\*

**Ammonium acetate,  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$**  (M.W. 77).—Dissolve 231 grams of the salt in 1 litre of water ... .. 3N

**Ammonium carbonate** (the commercial salt is a mixture of  $\text{NH}_4\text{HCO}_3$  and  $\text{NH}_4\text{CO}_2\text{NH}_2$ ).—Dissolve 160 grams of the salt in a mixture of 140 ml. of concentrated ammonia solution and 860 ml. of water ... .. 4N

**Ammonium chloride,  $\text{NH}_4\text{Cl}$**  (M.W. 53.5).—Dissolve 270 grams of the salt in 1 litre of water... 5N

**Ammonium nitrate,  $\text{NH}_4\text{NO}_3$**  (M.W. 80).—Dissolve 80 grams of the salt in 1 litre of water ... N

**Ammonium oxalate,  $(\text{NH}_4)_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}$**  (M.W. 142).—Dissolve 35 grams of the crystalline salt in 1 litre of water ... .. 0.5N

**Ammonium sulphate,  $(\text{NH}_4)_2\text{SO}_4$**  (M.W. 132).—Dissolve 132 grams of the salt in 1 litre of water 2N

**Ammonium thiocyanate,  $\text{NH}_4\text{SCN}$**  (M.W. 76).—Dissolve 38 grams of the salt in 1 litre of water ... .. 0.5N

**Yellow ammonium sulphide solution,  $(\text{NH}_4)_2\text{S}_x$ .**—Use the solution available commercially. It may be prepared, if desired, as follows. Saturate 150 ml. of concentrated ammonia solution with  $\text{H}_2\text{S}$ , keeping the solution cold; add 10 grams of flowers of sulphur and 250 ml. of concentrated ammonia solution, shake until the sulphur has dissolved and dilute to 1 litre ... 6N

\* The common reagents chlorine water, bromine water, iodine solution and hydrogen sulphide water are included here.

*Approximate  
normality*

**Colourless ammonium sulphide solution,  $\text{NH}_4\text{HS}$ .**—Saturate 200 ml. of concentrated ammonia solution cooled in ice water with  $\text{H}_2\text{S}$ , add an equal volume of concentrated ammonia solution and dilute with water to 1 litre. This solution is prepared as required ... ..

6N

**Barium chloride,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  (M.W. 244).**—Dissolve 61 grams of the salt in 1 litre of water ...

0.5N

**Bromine water,  $\text{Br}_2$  (M.W. 160).**—A saturated aqueous solution is prepared by shaking 35 grams or 11 ml. of liquid bromine with water. Add more bromine, if necessary, to ensure a slight excess.

**Calcium chloride,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  (M.W. 219).**—Dissolve 55 grams of the hydrated salt in 1 litre of water ... ..

0.5N

**Calcium sulphate,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (M.W. 172).**—Shake 3 grams of the salt with 1 litre of water; filter or decant the saturated solution after several hours ... ..

0.03N

**Chlorine water,  $\text{Cl}_2$  (M.W. 71).**—Saturate 250 ml. of water with chlorine. The chlorine may be generated by dropping concentrated  $\text{HCl}$  upon  $\text{KMnO}_4$ . Preserve in a dark-coloured bottle. The solution contains 6.5 grams of  $\text{Cl}_2$  per litre.

**Cobalt nitrate,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (M.W. 291).**—Dissolve 44 grams of the salt in 1 litre of water ...

0.3N

**Copper sulphate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (M.W. 249.5).**—Dissolve 125 grams of the salt in 1 litre of water containing 3 ml. of concentrated sulphuric acid ...

0.5N  
(as oxidant)

**Ferric chloride,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (M.W. 270).**—Dissolve 135 grams of the hydrated salt in 1 litre of water containing 20 ml. of concentrated  $\text{HCl}$  ...

0.5N  
(as oxidant)

**Ferrous sulphate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (M.W. 277).**—Dissolve 140 grams of the salt in 1 litre of water containing 7 ml. of concentrated  $\text{H}_2\text{SO}_4$  ... ..

0.5N  
(as reductant)

**Hydrogen sulphide solution,  $\text{H}_2\text{S}$  (M.W. 34).**—Saturate 250 ml. of water with  $\text{H}_2\text{S}$  gas derived from a Kipp's apparatus. The solution contains approximately 4.2 grams of  $\text{H}_2\text{S}$  per litre ...

0.05N

Approximate  
normality

**Iodine solution,  $I_2$  (M.W. 254).**—Dissolve 12.7 grams of iodine in a solution of 20 grams of pure KI in 30 ml. of water, and dilute to 1 litre with water ... ..

0.1N

**Lead acetate,  $Pb(C_2H_3O_2)_2 \cdot 3H_2O$  (M.W. 379).**—Dissolve 95 grams of the salt in 1 litre of water

0.5N

**Magnesium sulphate,  $MgSO_4 \cdot 7H_2O$  (M.W. 246).**—Dissolve 62 grams of the salt in 1 litre of water ... ..

0.5N

**Mercuric chloride,  $HgCl_2$  (M.W. 272).**—Dissolve 27 grams of the salt in 1 litre of water ...

0.2N

**Potassium chromate,  $K_2CrO_4$  (M.W. 194).**—Dissolve 49 grams of the salt in 1 litre of water ...

0.5N

(as precipitant)

**Potassium cyanide, KCN (M.W. 65).**—Dissolve 32.5 grams of the salt in 1 litre of water (*POISONOUS*) ... ..

0.5N

**Potassium ferricyanide,  $K_3[Fe(CN)_6]$  (M.W. 329).**—Dissolve 55 grams of the salt in 1 litre of water ... ..

0.5N

(as precipitant)

**Potassium ferrocyanide,  $K_4[Fe(CN)_6] \cdot 3H_2O$  (M.W. 422).**—Dissolve 53 grams of the salt in 1 litre of water ... ..

0.5N

(as precipitant)

**Potassium iodide, KI (M.W. 166).**—Dissolve 83 grams of the salt in 1 litre of water ... ..

0.5N

**Potassium permanganate,  $KMnO_4$  (M.W. 316).**—Dissolve 3.2 grams of the salt in 1 litre of water; filter through glass wool ... ..

0.1N

(as oxidant)

**Potassium thiocyanate, KSCN (M.W. 97).**—Dissolve 49 grams of the salt in 1 litre of water ...

0.5N

**Silver nitrate,  $AgNO_3$  (M.W. 170).**—Dissolve 17 grams of the salt in 1 litre of water ... ..

0.1N

**Silver sulphate,  $Ag_2SO_4$  (M.W. 312).**—Dissolve 8 grams of the salt in 1 litre of water. This is nearly a saturated solution ... ..

0.05N

**Sodium acetate,  $Na \cdot C_2H_3O_2 \cdot 3H_2O$  (M.W. 136).**—Dissolve 408 grams of the crystallised salt in 1 litre of water ... ..

3N

Approximate  
normality

**Sodium carbonate,  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  (M.W. 286).**—Dissolve 430 grams of the crystallised salt in 1 litre of water ... ..

3N

**Disodium hydrogen phosphate  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  (M.W. 358).**—Dissolve 120 grams of the salt in 1 litre of water ... ..

N

**Stannous chloride,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (M.W. 226).**—Dissolve 56 grams of the salt in 100 ml. of concentrated HCl and dilute to 1 litre. Keep a few pieces of tin in the bottle to prevent oxidation ...

0.5N

**Zinc Nitrate,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (M.W. 297).**—Dissolve 150 grams of the salt in 1 litre of water

0.5N

### SPECIAL REAGENTS

Experimental details for the preparation of many of the special, largely organic, reagents are given in the text; these can be located by reference to the Index. Some reagents, which are required for macro and semimicro analysis and which are not described in detail in the text, are collected below.

**Ammonium molybdate reagent.**—*Method A.* Dissolve 45 grams of the commercial salt  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  (a paramolybdate) or 40 grams of pure molybdenum trioxide  $\text{MoO}_3$  in a mixture of 70 ml. of concentrated ammonia solution and 140 ml. of water; when solution is complete, add it very slowly and with vigorous stirring to a mixture of 250 ml. of concentrated nitric acid and 500 ml. of water; dilute to 1 litre. Allow to stand 1–2 days and decant the clear solution.

*Method B.* Dissolve 45 grams of pure commercial ammonium molybdate in a mixture of 40 ml. of concentrated ammonia solution and 60 ml. of water, add 120 grams of ammonium nitrate and dilute to 1 litre with water.

The alkaline solution of ammonium molybdate keeps better than does the nitric acid solution; there is little tendency for the separation of solid. Before using the alkaline solution, it is important to ensure that the test solution contains a slight excess of nitric acid.

**Dimethylglyoxime reagent.**—Dissolve 1 gram of dimethylglyoxime in 100 ml. of rectified spirit (95 per cent ethyl alcohol).

**Fehling's solution.**—*Solution A* (blue): dissolve 34.6 grams of pure copper sulphate  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in distilled water and dilute to 500 ml.

*Solution B* (colourless): dissolve 173 grams of sodium potassium tartrate (Rochelle salt) and 50 grams of pure sodium hydroxide in water, and dilute to 500 ml. Alternatively, dissolve 121 grams of pure sodium hydroxide and 93.1 grams of pure tartaric acid in water, and then dilute the solution to 500 ml.

Mix equal volumes of solutions *A* and *B* immediately before use.

**Formaldehyde.**—Dilute the commercial 40 per cent solution (1 part) with water (7 parts).

**Fuchsin solution.**—Dissolve 0.15 gram of fuchsin in 100 ml. of water.

**Hydrogen peroxide.**—Use the commercial “10-volume” or 3 per cent solution. The “20-,” “40-” and “100-volume” solutions are also commercial products.

**Indigo solution.**—Gently warm 1 gram of indigo with 12 ml. of concentrated sulphuric acid, allow to stand for 48 hours and pour into 240 ml. of water. Filter, if necessary.

**Magnesia mixture.**—Dissolve 100 grams of magnesium chloride  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and 100 grams of ammonium chloride in water, add 50 ml. of concentrated ammonia solution and dilute to 1 litre with distilled water.

**Magnesium nitrate reagent.**—Dissolve 130 grams of magnesium nitrate  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 240 grams of ammonium nitrate in water, add 15–20 ml. of concentrated ammonia solution and dilute with water to 1 litre.

**Manganous chloride reagent.**—Add powdered manganous chloride  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  to concentrated hydrochloric acid until, after shaking, it no longer dissolves, *i.e.* prepare a saturated solution.

**Sodium cobaltinitrite solution.**—Dissolve 17 grams of the pure (*e.g.* analytical reagent quality) salt  $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$  in 250 ml. of water.

Alternatively, the solution may be prepared as follows. Dissolve 7.5 grams of cobalt nitrate  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in 30 ml. of water; dissolve 60 grams of sodium nitrite in 30 ml. of water; mix the two solutions with vigorous stirring and add 15 ml. of



glacial acetic acid, stir, dilute to 250 ml., allow to stand and filter. The solution should not be kept for more than 3–4 weeks as it is somewhat unstable.

**Sodium hypochlorite solution.**—The commercial product contains 10–14 per cent (w/v) of available chlorine. For most purposes, this must be diluted with an equal volume of water.

**Sodium nitroprusside solution.**—Prepare a solution as required by dissolving a crystal (about the size of a pea) in 5 ml. of water.

**Starch solution.**—Triturate 0.5 gram of soluble starch with a little cold water into a thin paste, and add 25 ml. of boiling water. Boil until a clear solution is obtained (5 minutes). This solution should be freshly prepared as required. A more stable starch solution is obtained by adding 0.5 gram of potassium iodide and 2–3 drops of chloroform.

A more satisfactory “starch solution” for use as an indicator is prepared as follows.\* Mix 5.0 grams of powdered sodium starch glycollate with 1–2 ml. of ethyl alcohol, add 100 ml. of cold water and boil for a few minutes with vigorous stirring. This 5 per cent stock solution is stable for many months; it is diluted to 0.1 per cent strength when required for use.

**Zirconyl nitrate reagent (for fluoride test).**—Dissolve 0.1 gram of zirconyl nitrate in 20 ml. of concentrated hydrochloric acid, and dilute with water to 100 ml.

**Zirconyl nitrate reagent (for phosphate separations).**—Heat 10 grams of commercially pure “zirconium nitrate”† { $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ } and 100 ml. of *N* nitric acid (prepared from 6.2 ml. of concentrated nitric acid diluted to 100 ml.) to the boiling point with constant stirring. Allow any undissolved solid to settle during 24 hours, and then decant the clear solution.

## SOLVENTS

Amyl acetate, $\text{CH}_3\text{COOC}_5\text{H}_{11}$	Ethyl alcohol (rectified spirit 95%), $\text{C}_2\text{H}_5\text{OH}$
Amyl alcohol, $\text{C}_5\text{H}_{11}\text{OH}$	Methyl alcohol (acetone free), $\text{CH}_3\text{OH}$
Carbon disulphide, $\text{CS}_2$	Ethyl ether, $(\text{C}_2\text{H}_5)_2\text{O}$
Carbon tetrachloride, $\text{CCl}_4$	Triethanolamine, $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$
Chloroform, $\text{CHCl}_3$	

\* For preparation of sodium starch glycollate, see Vogel, *Text Book of Quantitative Inorganic Analysis*, Second Edition, 1951, p. 332.

† Some commercial samples of “pure” zirconyl nitrate contain small amounts of ferric nitrate. A test for iron should therefore be made before preparing the solution.

## SOLID REAGENTS

Aluminium (turnings or foil), Al	Potassium nitrite, $\text{KNO}_2$
Ammonium chloride, $\text{NH}_4\text{Cl}$	Potassium iodide, KI
Ammonium nitrate, $\text{NH}_4\text{NO}_3$	Potassium permanganate, $\text{KMnO}_4$
Ammonium thiocyanate, $\text{NH}_4\text{SCN}$	Potassium persulphate, $\text{K}_2\text{S}_2\text{O}_8$
Asbestos fibre, for filters	Silica (precipitated), $\text{SiO}_2$
Borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	Sodium acetate (fused), $\text{Na} \cdot \text{C}_2\text{H}_3\text{O}_2$
Calcium chloride, $\text{CaCl}_2$	Sodium bicarbonate, $\text{NaHCO}_3$
Calcium fluoride, $\text{CaF}_2$	Sodium bismuthate, $\text{NaBiO}_3$
Copper (foil or turnings), Cu	Sodium bitartrate, $\text{NaH} \cdot \text{C}_4\text{H}_4\text{O}_6$
Devarda's alloy (powder)	Sodium hydroxide, NaOH
Ferrous sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	Sodium nitrite, $\text{NaNO}_2$
Fusion mixture, $\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$	Sodium nitroprusside, $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$
Glass wool	Sodium perborate, $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$
Iron (wire or powder), Fe	Sodium sulphite, $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$
Lead dioxide (Mn free), $\text{PbO}_2$	Sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$
Litmus paper (red and blue)	Stannic chloride, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$
Manganese dioxide (precipitated), $\text{MnO}_2$	Stannous chloride, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$
Methyl violet paper	Starch (soluble)
Microcosmic salt, $\text{Na}(\text{NH}_4)\text{HPO}_4 \cdot 4\text{H}_2\text{O}$	Starch-iodide paper
Potassium bisulphate, $\text{KHSO}_4$	Sulphur (flowers), S
Potassium carbonate, $\text{K}_2\text{CO}_3$	Tartaric acid, $\text{H}_2 \cdot \text{C}_4\text{H}_4\text{O}_6$
Potassium chlorate, $\text{KClO}_3$	Tin (pure foil), Sn
Potassium cyanide, KCN	Turmeric paper
Potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$	Zinc (20 mesh), Zn
Potassium nitrate, $\text{KNO}_3$	

pH Indicator papers (narrow range: 2.5-4.0, 4.0-5.5, 5.5-7.0, 7.0-8.5, 8.5-10.0; wide range: 2.0-10.5).

## A, 3.

## TEST SOLUTIONS

In order that the student may be able to judge the relative proportions of the constituents of mixtures from the size of precipitates, it is essential that he employs solutions of known strengths from the very outset. The test solutions described below contain 10 milligrams of the cation or anion per ml. If desired, stock solutions containing 100 milligrams per ml. may be prepared (provided the solubility of the salt is sufficiently high) and these subsequently diluted. *Pure* chemicals should be employed for the preparation of these solutions.

The cations are arranged in the order of the Groups; the anions in the order in which they are described in Chapter IV.

## CATIONS

<i>Cation</i>	<i>Formula of dry salt</i>	<i>Grams of salt per litre of solution</i>	<i>Special precautions in preparation of the solution</i>
Hg <sub>2</sub> <sup>++</sup> (ous)	Hg <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	14.0	Use 100 ml. of dilute HNO <sub>3</sub> .
Ag <sup>+</sup>	AgNO <sub>3</sub>	15.8	
Pb <sup>++</sup>	Pb(NO <sub>3</sub> ) <sub>2</sub>	16.0	Use 5 ml. of dilute HNO <sub>3</sub> .
	or Pb(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	18.3	Use 5 ml. of dilute H.C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> .
Hg <sup>++</sup> (ic)	HgCl <sub>2</sub>	13.5	
Bi <sup>+++</sup>	Bi(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O	23.2	Dissolve salt in 100 ml. of dilute HNO <sub>3</sub> and dilute to 1 litre.
Cu <sup>++</sup>	CuSO <sub>4</sub> ·5H <sub>2</sub> O	39.3	Use 5 ml. of dilute H <sub>2</sub> SO <sub>4</sub> .
	or CuCl <sub>2</sub> ·2H <sub>2</sub> O	26.8	Use 5 ml. of dilute HCl.
Cd <sup>++</sup>	3CdSO <sub>4</sub> ·8H <sub>2</sub> O	22.8	Use 5 ml. of dilute H <sub>2</sub> SO <sub>4</sub> .
	or Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	27.8	Use 5 ml. of dilute HNO <sub>3</sub> .
As (ous)	As <sub>2</sub> O <sub>3</sub>	13.2	Dissolve in hot water containing 20 ml. of dilute HCl and dilute to 1 litre.
As (ic)	As <sub>2</sub> O <sub>5</sub>	15.3	As for arsenious compound.
	or Na <sub>2</sub> HAsO <sub>4</sub> ·12H <sub>2</sub> O	53.7	
Sb (ous)	SbCl <sub>3</sub>	18.8	Dissolve in 500 ml. of dilute HCl and dilute to 1 litre.
Sb (ic)	SbCl <sub>5</sub>	24.5	As for antimonious compound.
Sn <sup>++</sup> (ous)	SnCl <sub>2</sub> ·2H <sub>2</sub> O	19.0	Dissolve in 100 ml. of concentrated HCl and dilute to 1 litre.
Sn <sup>++++</sup> (ic)	SnCl <sub>4</sub> ·5H <sub>2</sub> O	29.5	Dissolve in 500 ml. of dilute HCl and dilute to 1 litre.
Fe <sup>++</sup> (ous)	FeSO <sub>4</sub> ·(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O	70.3	Use 20 ml. of dilute H <sub>2</sub> SO <sub>4</sub> .
Fe <sup>+++</sup> (ic)	FeCl <sub>3</sub> ·6H <sub>2</sub> O	48.4	Use 50 ml. of dilute HCl.
Cr <sup>+++</sup>	CrCl <sub>3</sub> ·6H <sub>2</sub> O	51.2	Use 50 ml. of dilute HCl.
	or K <sub>2</sub> SO <sub>4</sub> ·Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·24H <sub>2</sub> O	96.0	Use 50 ml. of dilute H <sub>2</sub> SO <sub>4</sub> .
Al <sup>+++</sup>	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·18H <sub>2</sub> O	123.5	Use 20 ml. of dilute H <sub>2</sub> SO <sub>4</sub> .
	or K <sub>2</sub> SO <sub>4</sub> ·Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·24H <sub>2</sub> O	175.9	Use 20 ml. of dilute H <sub>2</sub> SO <sub>4</sub> .
Co <sup>++</sup>	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	49.4	
Ni <sup>++</sup>	NiSO <sub>4</sub> ·7H <sub>2</sub> O	47.8	
	or NiCl <sub>2</sub> ·6H <sub>2</sub> O	40.5	
Mn <sup>++</sup>	MnSO <sub>4</sub> ·4H <sub>2</sub> O	40.7	
	or MnCl <sub>2</sub> ·4H <sub>2</sub> O	36.0	
Zn <sup>++</sup>	ZnSO <sub>4</sub> ·7H <sub>2</sub> O	44.0	
	or Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	45.5	
Ba <sup>++</sup>	BaCl <sub>2</sub> ·2H <sub>2</sub> O	17.8	
	or Ba(NO <sub>3</sub> ) <sub>2</sub>	19.0	
Sr <sup>++</sup>	SrCl <sub>2</sub> ·6H <sub>2</sub> O	30.4	
	or Sr(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	32.4	
Ca <sup>++</sup>	CaCl <sub>2</sub> ·2H <sub>2</sub> O	36.7	
	or Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	58.9	

## Cations (contd.)

Cation	Formula of dry salt	Grams of salt per litre of solution	Special precautions in preparation of the solution
Mg <sup>++</sup>	MgSO <sub>4</sub> ·7H <sub>2</sub> O or Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	101.4 105.4	
K <sup>+</sup>	KCl or KNO <sub>3</sub>	19.1 25.9	
Na <sup>+</sup>	NaCl or NaNO <sub>3</sub>	25.4 37.0	
NH <sub>4</sub> <sup>+</sup>	NH <sub>4</sub> Cl or NH <sub>4</sub> NO <sub>3</sub>	29.7 44.4	

*Note.* If a slightly turbid solution is obtained with the cations of Groups IIIB, IV and Mg, about 5 ml. per litre of the dilute acid, corresponding to the anion of the salt, should be added.

## ANIONS

Anion	Formula of salt	Grams of salt per litre of solution
CO <sub>3</sub> <sup>-</sup>	Na <sub>2</sub> CO <sub>3</sub> ·10H <sub>2</sub> O	49.3
SO <sub>3</sub> <sup>-</sup>	Na <sub>2</sub> SO <sub>3</sub> ·7H <sub>2</sub> O*	31.5
S <sub>2</sub> O <sub>3</sub> <sup>-</sup>	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O*	22.2
S <sup>-</sup>	Na <sub>2</sub> S·9H <sub>2</sub> O	75.1
NO <sub>2</sub> <sup>-</sup>	NaNO <sub>2</sub> *	15.0
CN <sup>-</sup>	KCN	25.0
CNO <sup>-</sup>	KCNO	19.3
SCN <sup>-</sup>	KSCN	16.9
[Fe(CN) <sub>6</sub> ] <sup>-</sup>	K <sub>4</sub> [Fe(CN) <sub>6</sub> ]·3H <sub>2</sub> O	19.9
[Fe(CN) <sub>6</sub> ] <sup>-</sup>	K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	15.5
Cl <sup>-</sup>	NaCl	16.5
Br <sup>-</sup>	KBr	14.9
I <sup>-</sup>	KI	13.1
F <sup>-</sup>	NaF	22.1
AsO <sub>3</sub> <sup>-</sup> or AsO <sub>3</sub> <sup>-</sup> (arsenite)	NaAsO <sub>2</sub>	12.0
AsO <sub>4</sub> <sup>-</sup> (arsenate)	Na <sub>2</sub> HAsO <sub>4</sub> ·7H <sub>2</sub> O	22.5
NO <sub>3</sub> <sup>-</sup>	NaNO <sub>3</sub>	13.7
ClO <sub>3</sub> <sup>-</sup>	KClO <sub>3</sub>	14.7
BrO <sub>3</sub> <sup>-</sup>	KBrO <sub>3</sub>	13.1
IO <sub>3</sub> <sup>-</sup>	KIO <sub>3</sub>	12.2
ClO <sub>4</sub> <sup>-</sup>	KClO <sub>4</sub>	12.3
BO <sub>2</sub> <sup>-</sup> (borate)	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O	22.5
SO <sub>4</sub> <sup>-</sup>	Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O	33.6
SiO <sub>3</sub> <sup>-</sup>	Na <sub>2</sub> SiO <sub>3</sub>	16.1
[SiF <sub>6</sub> ] <sup>-</sup> (silicofluoride)	Na <sub>2</sub> [SiF <sub>6</sub> ]	13.2
PO <sub>4</sub> <sup>-</sup>	Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O	37.7
HPO <sub>3</sub> <sup>-</sup> (phosphite)	Na <sub>2</sub> HPO <sub>3</sub> ·2H <sub>2</sub> O	27.0
H <sub>2</sub> PO <sub>2</sub> <sup>-</sup> (hypophosphite)	NaH <sub>2</sub> PO <sub>2</sub> ·H <sub>2</sub> O	16.3
CrO <sub>4</sub> <sup>-</sup>	K <sub>2</sub> CrO <sub>4</sub>	16.7
MnO <sub>4</sub> <sup>-</sup>	KMnO <sub>4</sub>	13.3
C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup> (acetate)	Na·C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ·3H <sub>2</sub> O	23.1
H·CO <sub>2</sub> <sup>-</sup> (formate)	H·CO <sub>2</sub> Na	13.5
C <sub>2</sub> O <sub>4</sub> <sup>-</sup> (oxalate)	Na <sub>2</sub> ·C <sub>2</sub> O <sub>4</sub>	15.2
C <sub>4</sub> H <sub>4</sub> O <sub>6</sub> <sup>-</sup> (tartrate)	NaK·C <sub>4</sub> H <sub>4</sub> O <sub>6</sub> ·4H <sub>2</sub> O	19.1
C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> <sup>-</sup> (citrate)	Na <sub>3</sub> ·C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> ·2H <sub>2</sub> O	15.6
C <sub>6</sub> H <sub>5</sub> O <sub>3</sub> <sup>-</sup> (salicylate)	C <sub>6</sub> H <sub>4</sub> (OH)CO <sub>2</sub> Na	11.7
C <sub>6</sub> H <sub>5</sub> O <sub>2</sub> <sup>-</sup> (benzoate)	C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> K	13.2
C <sub>4</sub> H <sub>4</sub> O <sub>2</sub> <sup>-</sup> (succinate)	C <sub>2</sub> H <sub>4</sub> (CO <sub>2</sub> Na) <sub>2</sub>	14.0

## A, 4.

## BUFFER SOLUTIONS

The following standards are suitable for the calibration of pH meters and for other purposes which require an accurate knowledge of pH.

Solution	pH at		
	12°C	25°C	38°C
0.1M $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	—	1.48	1.50
0.1M HCl + 0.09M KCl	—	2.07	2.08
Saturated solution of potassium hydrogen tartrate, $\text{KHC}_4\text{H}_4\text{O}_6$	—	3.57	—
0.05M potassium hydrogen phthalate, $\text{KHC}_8\text{H}_4\text{O}_4$	4.000 (15°C)	4.005	4.015
0.1M $\text{CH}_3\text{COOH}$ + 0.1M $\text{CH}_3\text{COONa}$	4.65	4.64	4.65
0.025M $\text{KH}_2\text{PO}_4$ + 0.025M $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	—	6.85	6.84
0.05M $\text{Na}_2\text{B}_4\text{O}_7 \cdot 12\text{H}_2\text{O}$	—	9.18	9.07

Solutions of known pH for colorimetric determinations are conveniently prepared by mixing appropriate volumes of certain standard solutions. The compositions of a number of typical buffer solutions are given below.

**pH Range: 1.40–2.20 at 25°C (German and Vogel, 1937)**

X ml. of 0.1M p-toluenesulphonic acid monohydrate (19.012 grams per litre) and Y ml. of 0.1M sodium p-toluenesulphonate (19.406 grams per litre), diluted to 100.0 ml.

X (ml.)	Y (ml.)	pH	X (ml.)	Y (ml.)	pH
48.9	1.1	1.40	13.2	36.8	1.90
37.2	12.8	1.50	10.0	40.0	2.00
27.4	22.6	1.60	7.6	42.4	2.10
19.0	31.0	1.70	4.4	45.6	2.20
16.6	33.4	1.80			

**pH Range: 2.2-8.0 (McIlwaine, 1921)**

20.00 ml. mixtures of X ml. of 0.2M  $\text{Na}_2\text{HPO}_4$  and Y ml. of 0.1M citric acid.

X (ml.) $\text{Na}_2\text{HPO}_4$	Y (ml.) Citric acid	pH	X (ml.) $\text{Na}_2\text{HPO}_4$	Y (ml.) Citric acid	pH
0.40	19.60	2.2	10.72	9.28	5.2
1.24	18.76	2.4	11.15	8.85	5.4
2.18	17.82	2.6	11.60	8.40	5.6
3.17	16.83	2.8	12.09	7.91	5.8
4.11	15.89	3.0	12.63	7.37	6.0
4.94	15.06	3.2	13.22	6.78	6.2
5.70	14.30	3.4	13.85	6.15	6.4
6.44	13.56	3.6	14.55	5.45	6.6
7.10	12.90	3.8	15.45	4.55	6.8
7.71	12.29	4.0	16.47	3.53	7.0
8.28	11.72	4.2	17.39	2.61	7.2
8.82	11.18	4.4	18.17	1.83	7.4
9.35	10.65	4.6	18.73	1.27	7.6
9.86	10.14	4.8	19.15	0.85	7.8
10.30	9.70	5.0	19.45	0.55	8.0

pH Ranges: 2.2-3.8, 4.0-6.2, 5.8-8.0, 7.8-10.0 at 20°C

(Clark and Lubs, 1916)

- (A) pH 2.2-3.8. 50 ml. 0.2M  $KH_2PO_4$  + P ml. 0.2M HCl, diluted to 200 ml.  
 (B) pH 4.0-6.2. 50 ml. 0.2M  $KH_2PO_4$  + Q ml. 0.2M NaOH, diluted to 200 ml.  
 (C) pH 5.8-8.0. 50 ml. 0.2M  $KH_2PO_4$  + R ml. 0.2M NaOH, diluted to 200 ml.  
 (D) pH 7.8-10.0. 50 ml. 0.2M  $H_3BO_3$  and 0.2M KCl\* + S ml. 0.2M NaOH, diluted to 200 ml.

A		B		C		D	
P (ml.) HCl	pH	Q (ml.) NaOH	pH	R (ml.) NaOH	pH	S (ml.) NaOH	pH
46.60	2.2	0.40	4.0	3.66	5.8	2.65	7.8
39.60	2.4	3.65	4.2	5.64	6.0	4.00	8.0
33.00	2.6	7.35	4.4	8.55	6.2	5.90	8.2
26.50	2.8	12.00	4.6	12.60	6.4	8.55	8.4
20.40	3.0	17.50	4.8	17.74	6.6	12.00	8.6
14.80	3.2	23.65	5.0	23.60	6.8	16.40	8.8
9.95	3.4	29.75	5.2	29.54	7.0	21.40	9.0
6.00	3.6	35.25	5.4	34.90	7.2	26.70	9.2
2.65	3.8	39.70	5.6	39.34	7.4	32.00	9.4
—	—	43.10	5.8	42.74	7.6	36.85	9.6
—	—	45.40	6.0	45.17	7.8	40.80	9.8
—	—	47.00	6.2	46.85	8.0	43.90	10.0

\* That is, a solution containing 12.369 grams of  $H_3BO_3$  and 14.911 grams of KCl per litre.

**pH Range: 2.6–12.0 at 18°C—Universal Buffer Mixture***(Johnson and Lindsey, 1939)*

A mixture of 6.008 grams of A.R. citric acid, 3.893 grams of A.R. potassium dihydrogen phosphate, 1.769 grams of A.R. boric acid and 5.266 grams of pure diethylbarbituric acid is dissolved in water and made up to 1 litre. The pH values of mixtures of 100 ml. of this solution with various volumes (X) of 0.2N sodium hydroxide solution (free from carbonate) are tabulated below.

pH	X (ml.)	pH	X (ml.)	pH	X (ml.)
2.6	2.0	5.8	36.5	9.0	72.7
2.8	4.3	6.0	38.9	9.2	74.0
3.0	6.4	6.2	41.2	9.4	74.9
3.2	8.3	6.4	43.5	9.6	77.6
3.4	10.1	6.6	46.0	9.8	79.3
3.6	11.8	6.8	48.3	10.0	80.8
3.8	13.7	7.0	50.6	10.2	82.0
4.0	15.5	7.2	52.9	10.4	82.9
4.2	17.6	7.4	55.8	10.6	83.9
4.4	19.9	7.6	58.6	10.8	84.9
4.6	22.4	7.8	61.7	11.0	86.0
4.8	24.8	8.0	63.7	11.2	87.7
5.0	27.1	8.2	65.6	11.4	89.7
5.2	29.5	8.4	67.5	11.6	92.0
5.4	31.8	8.6	69.3	11.8	95.0
5.6	34.2	8.8	71.0	12.0	99.6



## A. 5. SOLUBILITIES OF SALTS AND BASES IN WATER AT 18°C\*

	K	Na	Li	Mg	Ba	Sr	Ca	Zn	Pb	Ag
Cl	32.95	35.86	77.79	55.81	37.24	51.09	73.19	203.9	1.49	$1.4 \times 10^{-4}$
Br	65.86	88.76	168.7	103.1	103.6	96.52	143.3	478.2	0.97	$1 \times 10^{-3}$
I	137.5	177.9	161.5	148.2	201.4	169.2	200.0	419.0	0.08	$3.0 \times 10^{-7}$
F	92.56	4.44	0.27	0.0076	0.16	0.012	0.0016	0.005	0.06	195.4
NO <sub>3</sub>	30.34	83.97	71.43	74.31	8.74	66.27	121.8	117.8	51.66	213.4
ClO <sub>3</sub>	6.6	97.16	313.4	126.4	35.42	174.9	179.3	183.9	150.6	12.25
BrO <sub>3</sub>	6.38	36.67	152.5	42.86	0.8	30.0	85.17	58.43	1.3	0.59
IO <sub>3</sub>	7.62	8.33	80.43	6.87	0.05	0.25	0.25	0.83	0.002	0.004
SO <sub>4</sub>	11.11	16.83	35.64	35.43	$2.3 \times 10^{-4}$	0.011	0.20	53.12	0.0041	0.55
CrO <sub>4</sub>	63.1	61.21	111.6	73.0	$3.8 \times 10^{-4}$	0.12	0.4	—	$2 \times 10^{-5}$	0.0025
C <sub>2</sub> O <sub>4</sub>	30.27	3.34	7.22	0.03	0.0086	0.0046	$5.6 \times 10^{-4}$	$7.9 \times 10^{-4}$	0.0001	0.0035
CO <sub>3</sub>	108.0	19.39	1.3	0.1	0.0023	0.0011	0.0013	—	0.0001	0.003
OH	142.9	116.4	12.04	0.001	3.7	0.77	0.17	0.0005	0.01	0.002 (?)

\* The solubilities are expressed in grams of anhydrous salt dissolved by 100 ml. of water.

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	9	13	17	21	26	30	34	38
											4	8	12	16	20	24	28	32	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	12	15	19	23	27	31	35
											4	7	11	15	19	22	26	30	33
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	11	14	18	21	25	28	32
											3	7	10	14	17	20	24	27	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	7	10	13	16	20	23	26	30
											3	7	10	12	16	19	22	25	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	28
											3	6	9	12	15	17	20	23	26
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	9	11	14	17	20	23	26
											3	5	8	11	14	16	19	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	10	13	16	19	22	24
											3	5	8	10	13	15	18	21	23
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	3	5	8	10	13	16	18	20	23
											3	5	7	10	12	15	17	19	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
											2	5	7	9	11	14	16	18	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
											2	4	6	8	11	13	15	17	19
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	16	18
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6929	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8

# LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	6	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8115	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	4	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9858	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9898	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	4	4

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
-00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	1	2	2
-01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	1	2	2
-02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	1	2	2
-03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	1	2	2
-04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	0	1	1	1	1	1	2	2
-05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	1	2	2	2
-06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	1	2	2	2
-07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	1	2	2	2
-08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	1	2	2	2
-09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	1	2	2	2
-10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	1	2	2	2
-11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	1	2	2	2	2
-12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	1	2	2	2	2
-13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	1	2	2	2	2
-14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	1	2	2	2	2
-15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	1	2	2	2	2
-16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	1	2	2	2	2
-17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	1	2	2	2	2
-18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	1	2	2	2	2
-19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	1	2	2	2	2
-20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	1	2	2	2	2
-21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	1	1	2	2	2	2
-22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	1	1	2	2	2	2
-23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	1	1	2	2	2	2
-24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	1	1	2	2	2	2
-25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	1	1	2	2	2	2
-26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	1	1	2	2	2	2
-27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	1	1	2	2	2	2
-28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	1	1	2	2	2	2
-29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	1	1	2	2	2	2
-30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	1	1	2	2	2	2
-31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	1	1	2	2	2	2
-32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	1	1	2	2	2	2
-33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	1	1	2	2	2	2
-34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	1	1	2	2	2	2	2
-35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	1	1	2	2	2	2	2
-36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	1	1	2	2	2	2	2
-37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	1	1	2	2	2	2	2
-38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	1	1	2	2	2	2	2
-39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	1	1	2	2	2	2	2
-40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	1	1	2	2	2	2	2
-41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	1	1	2	2	2	2	2
-42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	1	1	2	2	2	2	2
-43	2692	2698	2704	2710	2716	2722	2729	2735	2742	2748	1	1	1	1	2	2	2	2	2
-44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	1	1	2	2	2	2	2
-45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	1	1	2	2	2	2	2
-46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	1	1	2	2	2	2	2
-47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	1	1	2	2	2	2	2
-48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	1	1	2	2	2	2	2
-49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	1	1	2	2	2	2	2

# ANTILOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
-50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
-51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	4	5	6	7
-52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	4	5	6	7
-53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	4	5	6	7
-54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	4	5	6	7
-55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	4	5	6	7
-56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	4	5	6	7
-57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	4	5	6	7
-58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	4	5	6	7
-59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	4	4	5	6	7
-60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	5	6	7	8
-61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	5	6	7	8
-62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	5	6	7	8
-63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	5	6	7	8
-64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	5	6	7	8
-65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	5	6	7	8
-66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	5	6	7	9
-67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	5	6	7	9
-68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	5	5	6	7	9
-69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	4	5	5	6	7	9
-70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	6	7	8	9
-71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	6	7	8	10
-72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	6	7	8	10
-73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	2	4	5	6	6	7	8	10
-74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	6	7	8	10
-75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	7	8	9	10
-76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	7	8	9	11
-77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	7	8	10	11
-78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	7	8	10	11
-79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	7	8	10	11
-80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	7	8	10	12
-81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	8	9	11	12
-82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	8	9	11	12
-83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	8	9	11	13
-84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	8	9	11	13
-85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	8	9	10	12
-86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	8	9	10	12
-87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	9	10	12	14
-88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	9	10	12	14
-89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	9	10	12	14
-90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	9	10	12	15
-91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	9	10	12	15
-92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	9	9	10	12	15
-93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	9	9	10	12	15
-94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	9	9	10	12	15
-95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	9	9	10	12	15
-96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	9	9	10	12	15
-97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	9	9	10	12	15
-98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	9	9	10	12	15
-99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	9	9	10	12	15



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